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The Determination of Mercury in stack Gases of High SO2 Content by the Gold Amalgamation Technique

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The Determination of Mercury in Stack Gases of High SO_2 Content by the Gold Amalgamation Technique

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16. Abstracts: Elemental mercury, present in the reducing atmosphere of exhaust flue gases from a zinc smelter, may be quantitatively determined by the gold amalgamation technique. The gas sample may be taken isokinetically using a standard isokinetic stack sampling apparatus in which some of the impingers are replaced by a series of amalgamators, each containing 30 grams of gold chips. Several combinations of impingers and amalgamators were investigated to determine the optimum train configuration. Collection efficiency of the optimized train was found to approach 98-100%. Equations were derived for estimating the collection efficiency of the train from the relative distribution of mercury found on successive amalgamators. Sources of error and possible gold contamination are discussed. Analytical procedures for determining mercury concentration were studied including (1) $KMnO_4$ and ICl as oxidizing solutions, (2) direct aeration and reamalgamation, (3) air and nitrogen as the carrier gases, (4) magnesium perchlorate as a drying reagent, (5) the use of mixing chambers, and (6) use of a mercury vapor monitor instead of a modified atomic absorption spectrophotometer.

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The Determination of Mercury in Stack Gases of High SO_2 Content by the Gold Amalgamation Technique

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ABSTRACT

Elemental mercury, present in the reducing atmosphere of exhaust flue gases from a zinc smelter may be quantitatively determined by the gold amalgamation technique. This method avoids interferences by strongly reducing substances, such as SO_2, encountered in the direct application of the normally used wet oxidation techniques (e.g., ICl or $KMnO_4$ scrubbers) to these sources. The gas sample may be taken isokinetically using a standard isokinetic stack sampling apparatus in which some of the impingers are replaced by a series of amalgamators, each containing 30 grams of gold chips. After sampling, these amalgamators are removed from the sampling unit and the trapped mercury is fired by an induction furnace into a nitrogen stream which carries the revolatilized mercury into a solution of 3% $KMnO_4$ in 10% HNO_3, where it is oxidized and retained. The resulting solution is then analyzed for mercury by reduction with hydroxylamine hydrochloride and stannous chloride followed by direct aeration through a "mercury vapor monitor" which measures the absorbance at 253.7 nm. Mercury collected with the particulate portion of the sample may be determined by nitric acid digestion of the filter followed by reduction with stannous chloride and aeration.

Several combinations of impingers and amalgamators were investigated to determine the optimum train configuration. Collection efficiency of the optimized train was found to approach 98-100% and to be independent of the sampling rate in the range 0.3 to 0.8 CFM. Equations were

derived for estimating the collection efficiency of the train from the relative distribution of mercury found on successive amalgamators. The most crucial parameter affecting the collection efficiency was found to be the cleanness of the gold used. Sources of error and possible gold contamination are discussed. Analytical procedures for determining the mercury concentration were studied, including (1) $KMnO_4$ and ICl as oxidizing solutions, (2) direct aeration and reamalgamation, (3) air and nitrogen as the carrier gases, (4) the use of magnesium perchlorate as a drying reagent, (5) the use of mixing chambers, and (6) the utilization of a mercury vapor monitor as compared to a modified atomic absorption spectrophotometer. The recommended procedure for the determination of mercury in a stack gas using the method optimized in this study is presented in the appendix.

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INTRODUCTION

The discovery of unacceptable levels of mercury in water and certain foods has led to an increased concern over the possible pollution of the environment with mercury. The persistence of mercury and its tendency to accumulate in some parts of the ecological system are important aspects of the problem. These developments have stimulated interest in the analytical techniques for mercury and numerous improved methods have been published for its determination in foodstuffs, animal tissues, blood, urine, water, geological samples, sediment, pulp, soil and rocks. For many of these applications the flameless atomic absorption method (often combined with an amalgamation step to improve selectivity and sensitivity[1]) has been found faster, less cumbersome and more sensitive than the classical dithizone extraction method.

Although the U.S. Government has established maximum permissible levels for mercury in various foodstuffs and for plant effluent to streams, little data is available on the quantity of airborne mercury emitted from such sources as coal-fired power plants or smelting operations. Most coal has been shown to contain 0.05 to 0.50 ppm mercury[2] and a cross section of copper, zinc, and lead sulfide ores from the United

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[1] G.W. Kalb, The Determination of Mercury in Water and Sediment Samples by Flameless Atomic Absorption, Atomic Absorption Newsletter 9(4), pp. 84-87(1970).

[2] Personal Communication, ASTM Committee D5.21, Trace Element Task Group.

States has been analyzed for mercury showing a range of 0.05 to 300 ppm.[3] This naturally occurring mercury is volatilized during combustion and could result in the release of a significant quantity of mercury into the atmosphere.

The two methods ordinarily used for the determination of mercury in air are subject to massive interferences from the other components normally found in stack gases, particularly SO_2. Efforts to determine the mercury in stack gases by drawing the gas through a sampling train containing a liquid oxidizing agent (acidic $KMnO_4$ or ICl) have not been successful. The high SO_2 concentration in the sample reduces the oxidizer almost immediately, eliminating its ability to oxidize the mercury to the mercuric state. The direct measurement of mercury in air using a "mercury vapor monitor" is another widely used technique. The air sample is drawn between an ultraviolet source which emits the 253.7 nm mercury vapor resonance line and a photocell detector. The absorbance is measured and can be converted directly to mercury concentration; but the response is not specific since SO_2, most organic substances, smokes, and aerosols also absorb at this wavelength. An alternate method of mercury collection is needed for stack sampling; one which does not depend on the oxidation of mercury for entrapment. Such a method would enable longer sampling times to be used, even in

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[3]Personal Communication, David Patrick, Environmental Protection Agency, Research Triangle Park, North Carolina.

the presence of high SO_2 concentrations. Previous work by the authors[4,5] has shown that elemental mercury can be quantitatively collected from a stack gas sample by direct amalgamation onto gold. The mercury can then be revolatilized by heating and determined by any of several methods. Good recovery of mercury was obtained from the effluent gas of a coal-fired power plant and a zinc roaster where SO_2 concentrations averaged around 7-8%. Although recovery of mercury in this earlier work was generally good, the analytical method used (firing the gold in an air stream which carried the revolatilized mercury through a quartz cell positioned in the beam of an atomic absorption spectrophotometer) was too sensitive, limiting the feasible sampling time to 1-3 minutes, depending on the mercury concentration, and subject to interferences from any moisture, sulfuric acid mist or other substances which condensed on the gold during sampling. These problems limited the accuracy and reproducibility of the results obtained. The present work was undertaken to solve these problems and generally improve the practicality of the gold amalgamation method as applied to stack sampling. The goal of this work was threefold:

1. To develop a procedure which would allow a sampling time of at least 15 minutes at isokinetic rates (i.e., a sampling rate of 0.5 - 0.8 CFM, or under actual isokinetic conditions).

2. To obtain and show a collection efficiency of at least 95% for the mercury.

3. To perfect the method of firing the gold into an acidic $KMnO_4$ solution with subsequent analysis of aliquots of this solution by flameless atomic absorption.

These goals were successfully attained in this study.

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[4] G.W. Kalb and C. Baldeck, The Development of the Gold Amalgamation Sampling and Analytical Procedure for Investigation of Mercury in Stack Gases, Environmental Protection Agency Contract No. 68-02-0341 (1972).

[5] G.W. Kalb, The Adaptation of the Gold Amalgamation Sampling and Analytical Procedure for Investigation of Mercury in Stack Gases to High SO_2 Environments Observed in Smelters, Environmental Protection Agency Contract No. 68-02-0341 (1972).

LABORATORY INVESTIGATIONS

1 - Introduction

A previous study has shown that volatile mercury in smelter gases may be quantitatively collected on gold by an amalgamation reaction. (At the high temperatures (500°F) and the reducing atmospheres observed in smelter gases the mercury present will be in the elemental state.) The mercury was analyzed by firing the amalgam in an induction furnace and then monitoring the volatile mercury concentration by flameless atomic absorption. Standards were run after each sample to calibrate the instrument. Although the smelter investigated used an ore of relatively low mercury concentration, the mercury concentration was sufficiently high to limit the sampling time to one minute. Samples collected isokinetically for longer periods of time contained more mercury than could be analyzed by the system.

In order to obtain a representative sample a longer sampling period was required resulting in the otherwise arbitrary choice of a desired 15-minute sampling period. Sample splitting procedures and redesign of the optical system could not adequately desensitize the system, especially when it is realized that ores used in some smelters contain 300 times the mercury concentration observed in the smelter studied. As a result of this it was decided to revolatilize the mercury collected on the amalgam, absorbing the revolatilized mercury in an acidic permanganate or iodine monochloride solution. Aliquots of these solutions could then be diluted for analysis. It was the objective of this phase of the contract to study various methods for analyzing these solutions.

The mercury-gold amalgam obtained from sampling the stack gas is fired in a resistance or an induction furnace with a compressed gas stream carrying the mercury through a liquid absorption cell containing an iodine monochloride or acidic permanganate solution that quantitatively removes the mercury from the gas stream. An aliquot of this solution is then diluted to a satisfactory range for analysis. Procedures investigated for the analyses of these solutions included: (1) direct aeration of the reduced $KMnO_4$ or ICl solution into a flameless atomic absorption spectrophotometer, and (2) secondary amalgamation accompanied by the direct firing of the amalgam into a flameless atomic absorption spectrophotometer. These procedures were studied using both air and nitrogen as the carrier gases and with and without magnesium perchlorate as a drying reagent in the gas stream. Various mixing chambers were also investigated as an additional means of desensitizing the analytical method.

The second objective of this study was to determine the ultimate capacity of the gold for mercury. The results from this are to be used to determine the size and shape of the final amalgamator to be used in conjunction with the isokinetic sampler in obtaining the sample from the stack.

The final objective of the laboratory study was to develop a method for analyzing the filters containing the particulates collected during sampling.

2- Instrumental Methods

The instrumental methods were investigated by comparing their sensitivity and response with standard mercury in water solutions. 50 ml aliquots of the various mercury standards were reduced with 2 ml of a solution of 20% $SnCl_2$ in 50% HCl. These standards were then aerated, quickly volatilizing the reduced mercury. The air stream carried the mercury either directly into a quartz optical cell located in the path of an atomic absorption spectrophotometer operated at 254 nm (direct aeration) or onto gold (secondary amalgamation). In the latter use, the gold amalgamator was then fired in an induction furnace revolatilizing the mercury which was carried by the air stream into the optical path of the spectrophotometer. A model 303 Perkin-Elmer atomic absorption spectrophotometer and a Laboratory Data Control (LDC) Mercury Monitor were utilized for the study.

Figure 1 shows the relative response of the LDC Mercury Monitor with a 30 cm path length and the atomic absorption spectrophotometer with a 6-½ inch optical cell, using the direct aeration technique. The two units were operated at the same air flow (1.4 liters/minute). The LDC unit, operated at a 0.64 range (least sensitive available), shows an absorbance of 80 with a 1 µg mercury standard. The atomic absorption unit has a considerably lower sensitivity. Figure 2 illustrates a similar comparison, but with the secondary amalgamation method. The gold amalgams were fired at different temperatures (% variac setting) in the induction furnace. The secondary amalgamation

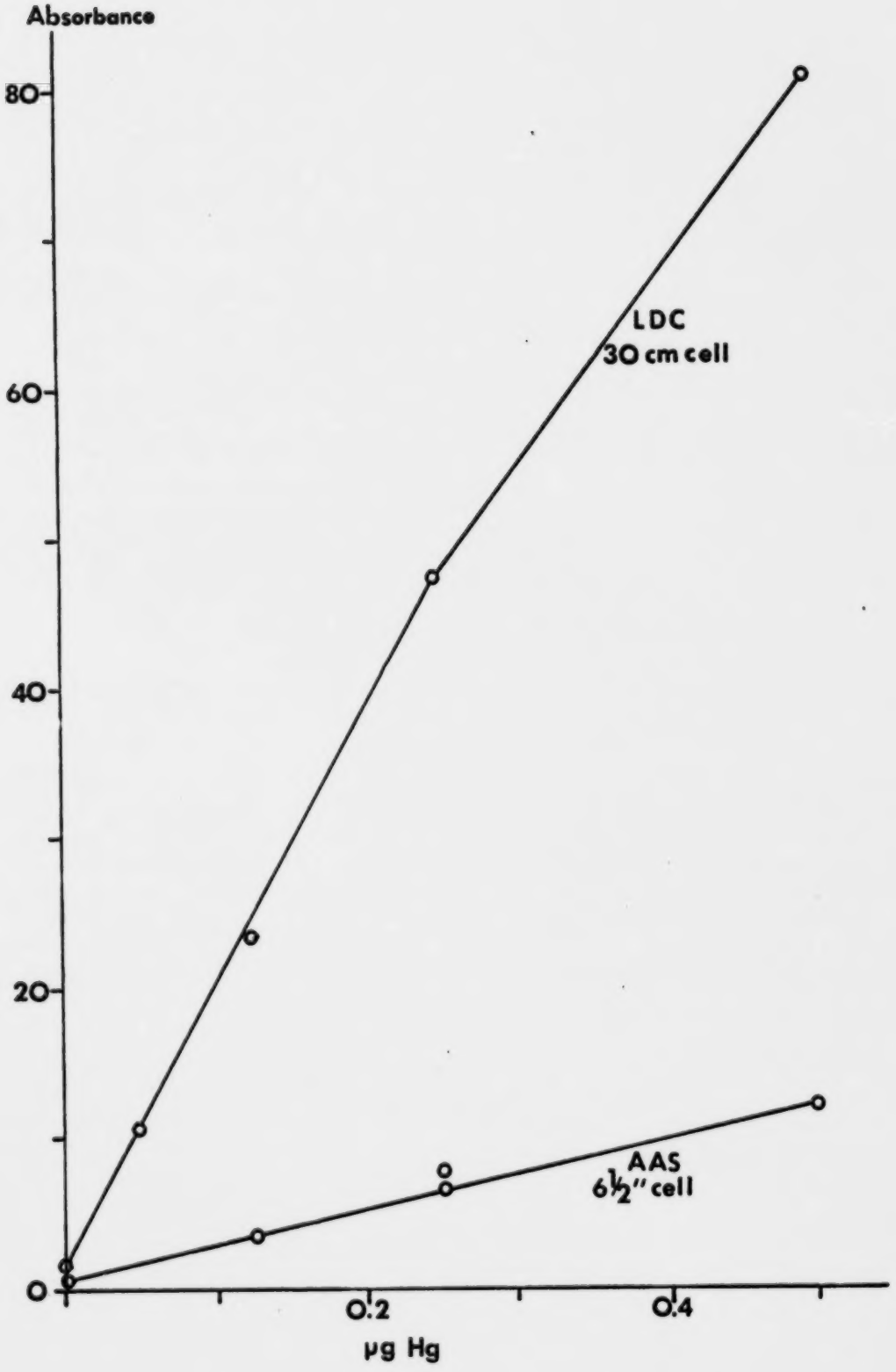

Figure 1. Relative Response of the LDC Mercury Monitor and an Atomic Absorption Spectrophotometer with a 6½ Inch Quartz Optical Cell using the Direct Aeration Technique.

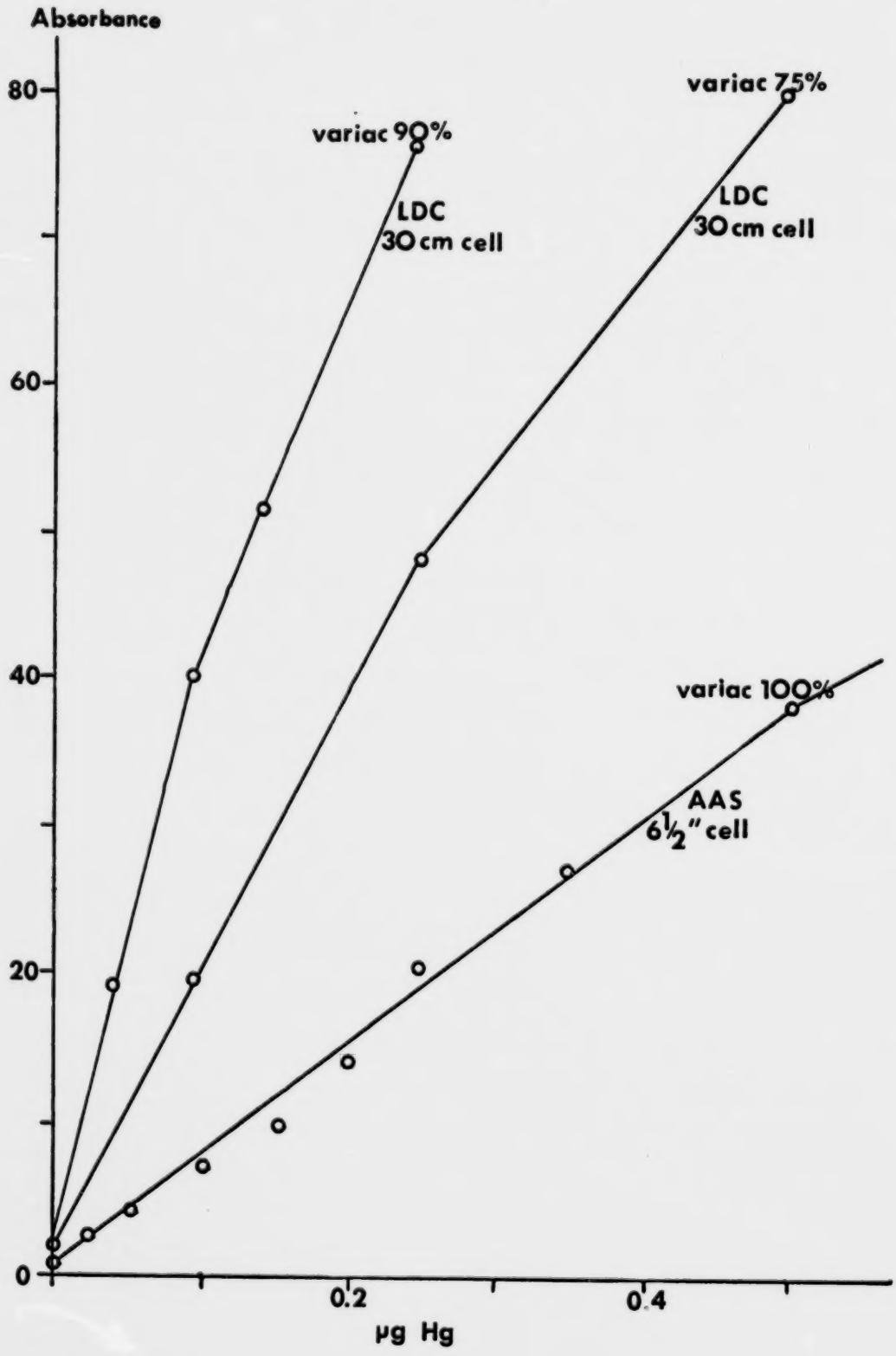

Figure 2. Relative Response of the LDC Mercury Monitor and an Atomic Absorption Spectrophotometer with a 6½ Inch Quartz Optical Cell using the Amalgamation Technique.

procedure, originally designed to eliminate interferences and increase sensitivity, is considerably more sensitive than the direct aeration method.

The LDC unit is, as would be expected, more sensitive than the atomic absorption spectrophotometer. The LDC unit in conjunction with amalgamation approaches the maximum limit of sensitivity. At the low mercury concentrations required to remain on scale there is considerable fluctuation in the absorbance values. The sensitivity of this method is such that it is useful only under optimum conditions. This appears to be because of temperature fluctuations in the optical cell due to the firing of the amalgam, resulting in an unstable equilibrium between the volatile materials and the cell walls. This, in conjunction with the high sensitivity due to the long cell, severely limits its usage.

Figures 3 and 4 illustrate the effect of mixing chambers on the sensitivity of the direct aeration and secondary amalgamation procedures. The two mixing chambers investigated, 150 ml and 270 ml gas collection tubes, did not significantly decrease the sensitivity with either the direct aeration or amalgamation techniques. They did improve the reproducibility of the peaks by decreasing the sharpness of the peak tip with both procedures. It is likely that utilizing the mixing chambers with the secondary amalgamation procedure will decrease the sudden thermal expansion of the gas, which could be responsible for the lack of reproducibility with the highly sensitive LDC Mercury Monitor.

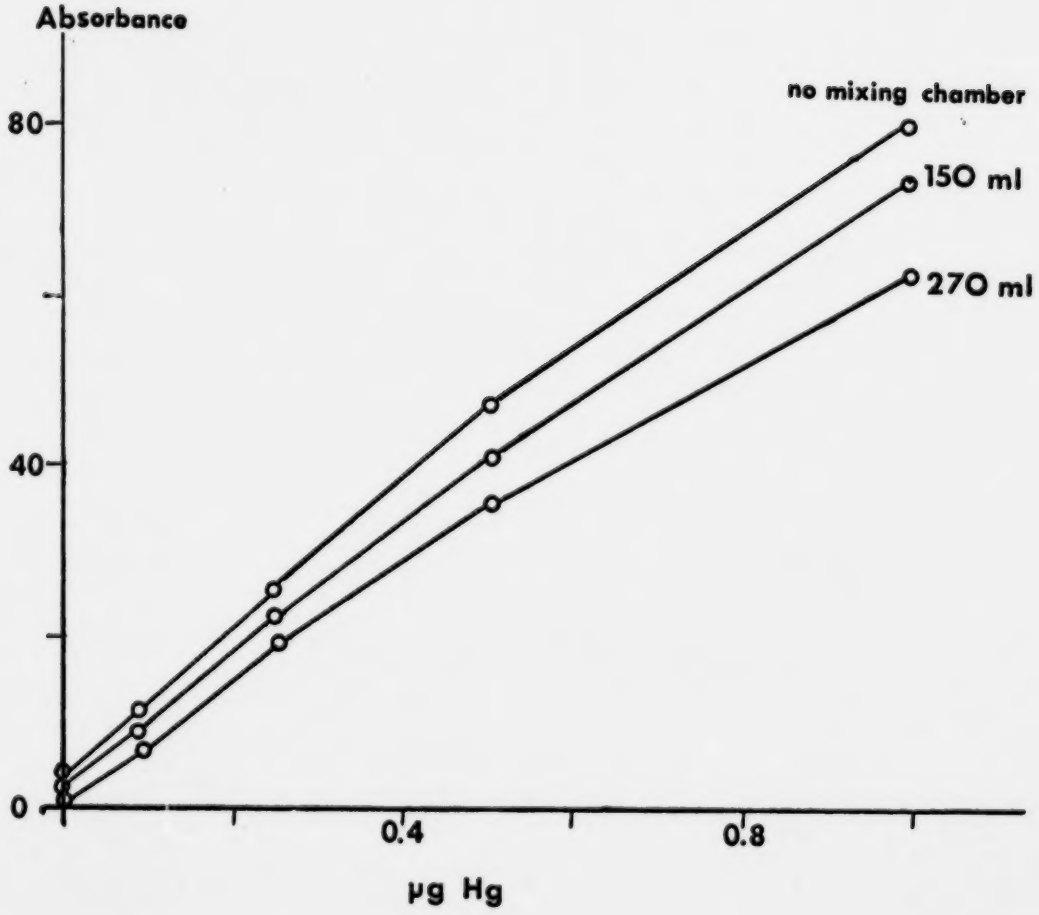

Figure 3. Effect of Mixing Chambers on Analytical Curves with the Direct Aeration Procedure.

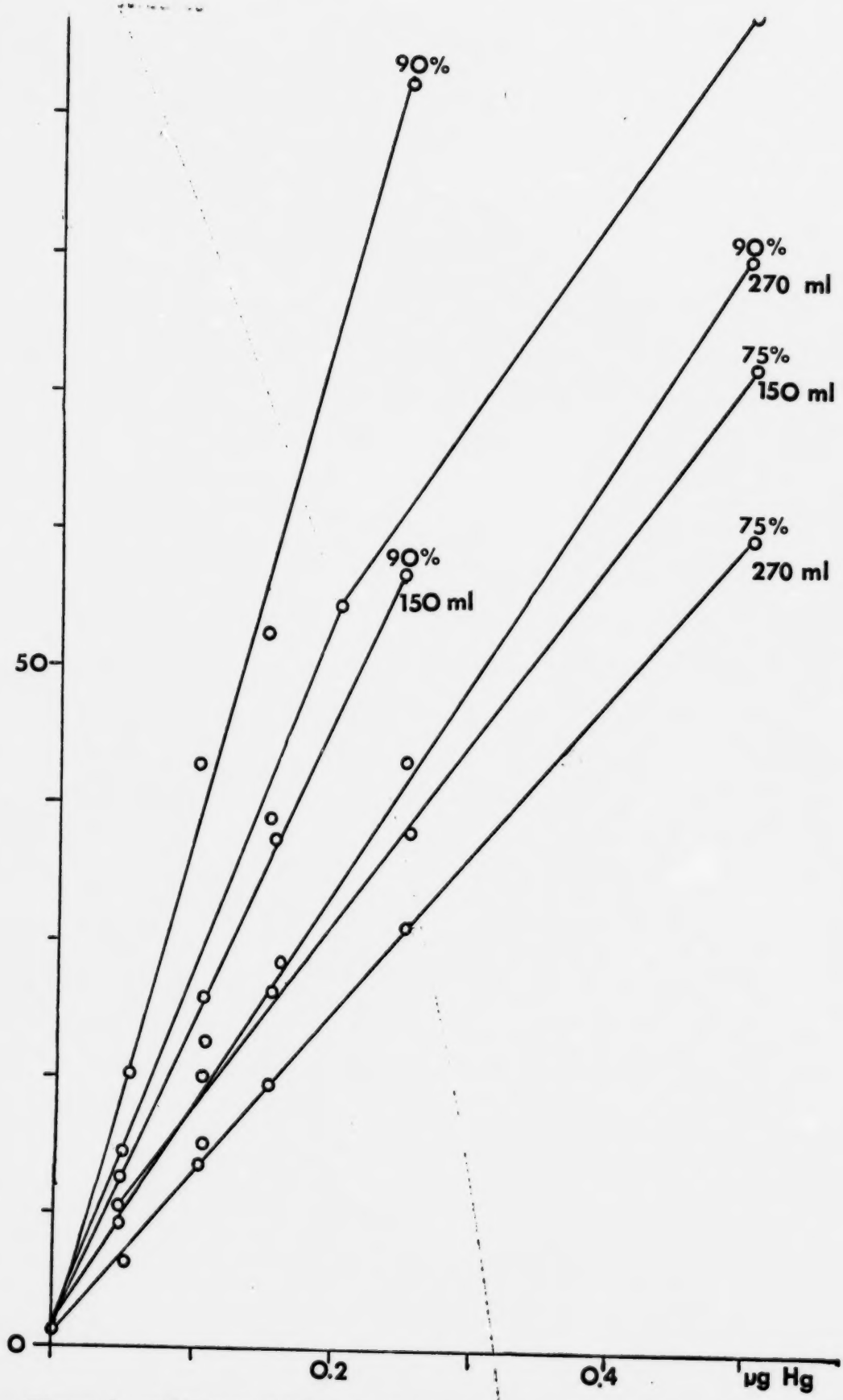

Figure 4. Effect of Mixing Chambers on Analytical Curves with Amalgamation.

The results of the instrumental analysis comparison has suggested that the secondary amalgamation procedure is unnecessary. The amalgamation procedure is designed to eliminate interferences and increase sensitivity. The primary amalgamation step utilized in the original collection of the stack gas sample and the desire to decrease the sensitivity, limits its usefulness unless an interference is found in the oxidizing solutions. The amalgamation procedure can be partially desensitized by lowering the firing temperature or the air flow rate. If the amalgamation procedure is adopted, it is recommended that the mixing cells should be used in conjunction with the 6-½ inch optical cell in the atomic absorption spectrophotometer. If the LDC Mercury Monitor is to be used, a shorter optical cell would be advantageous ($500.00). Considering the high mercury concentrations of the oxidizing solutions to be analyzed, the direct aeration procedure, utilizing either the LDC Monitor or the Perkin-Elmer atomic absorption spectrophotometer is recommended. With this procedure mixing chambers would not be required.

3- Oxidizing Solutions

The oxidizing solutions to be utilized in collecting the mercury at the field site are to be a 3% $KMnO_4$ solution in 10% concentrated nitric acid or a 0.1 N ICl solution. In practice these solutions would be diluted for final analyses. Due to the various dilutions that will be performed on the actual samples and as a check on any possible interferences, the laboratory study was performed with the above strength solutions. These solutions were then spiked with known amounts of

mercury before analyses. Analysis of mercury in water standards have been thoroughly investigated by this laboratory and were utilized for comparison with the oxidizing solutions, as well as to compare the various instrumental procedures.

a. $\underline{KMnO_4}$

The reactions responsible for the oxidation and reduction of mercury in the permanganate system are shown in Table 1. In acidic solutions the permanganate ion is a strong oxidizing reagent. The half reaction is

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{++} + 4H_2O \qquad E^\circ = 1.51$$

This half reaction only occurs in strongly acidic solutions (0.1 N or greater). In less acidic permanganate solutions

$$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O \qquad E^\circ = 1.695$$

In alkaline solutions

$$MnO_4^- + 2H_2O + 3e^- \rightleftharpoons MnO_2 + 4OH^- \qquad E^\circ = 0.588$$

In strongly alkaline solutions

$$MnO_4^- + e^- \rightleftharpoons MnO_4^= \qquad E^\circ = 0.564$$

Permanganate is unstable in the presence of Mn^{++}, but the reaction is very slow in acidic media

$$2MnO_4^- + 3Mn^{++} + 2H_2O \rightleftharpoons 5MnO_2 + 4H^+$$

TABLE 1

Half-Reactions Involved in the Oxidation-Reduction of Mercury*

	Potential
1. Oxidation of Mercury:	
$Hg^{o} \rightleftharpoons Hg^{++} + 2e^{-}$	-0.852
(Strong Acid) $Mn^{++} + 4H_2O \rightleftharpoons MnO_4^{-} + 8H^{+} + 5e^{-}$	-1.51
(Weak Acid) $MnO_2 + 2H_2O \rightleftharpoons MnO_4^{-} + 4H^{+} + 3e^{-}$	-1.695
2. Reduction of Excess MnO_4^{-} :	
(Strong Acid) $Mn^{++} + 4H_2O \rightleftharpoons MnO_4^{-} + 8H^{+} + 5e^{-}$	-1.51
(Weak Acid) $MnO_2 + 2H_2O \rightleftharpoons MnO_4^{-} + 4H^{+} + 3e^{-}$	-1.695
$Mn^{++} + 2H_2O \rightleftharpoons MnO_2 + 4H^{+} + 2e^{-}$	-1.23
$H_2NOH \cdot HCl \rightleftharpoons (NO_2, N_2O_4, HNO_2)$	
3. Reduction of Mercury:	
$Hg^{o} \rightleftharpoons Hg^{++} + 2e^{-}$	-0.852
$Sn^{++} + 6Cl^{-} \rightleftharpoons SnCl_6 + 2e^{-}$	-0.15
$N_2O_4 + 2H_2O \rightleftharpoons 2NO_3^{-} + 4H^{+} + 2e^{-}$	-0.9
$HNO_2 + 4H_2O \rightleftharpoons NO_3^{-} + 3H^{+} + 2e^{-}$	-0.94
$NO_2 + 2H_2O \rightleftharpoons NO_3^{-} + 4H^{+} + 3e^{-}$	-0.96

*H.A. Laitinen, "Chemical Analysis," McGraw-Hill Book Company, New York, N.Y., 1960.

This reaction would affect the length of storage of $KMnO_4$ solutions after the mercury has been collected. The overall reaction would be

$$5Hg^{o} + 2MnO_4^{-} + 16H^{+} \rightleftharpoons 5Hg^{++} + 2Mn^{++} + 8H_2O$$

The Mn^{++} would eventually lead to the deterioration of the permanganate.

MnO_2 catalyzes the decomposition of permanganate under acidic conditions resulting in the necessity of filtering fresh permanganate solutions. Any organic material present in the storage vessel will reduce the permanganate to MnO_2 resulting in autodecomposition. Acidic and alkaline solutions of permanganate are less stable than neutral solutions. MnO_2 will also form in the initial oxidation of the volatile mercury if the solution is not sufficiently acidic (see Table 1).

With the utilization of the permanganate system the excess permanganate (that not required to oxidize the mercury) is reduced with hydroxylamine hydrochloride. The half reactions are shown in Section 2 of Table 1. (The oxidation potential of the hydroxylamine hydrochloride is unknown, but would be between 0.9 and 1.23 volts.) The formation of Mn^{++} or MnO_2 is dependent upon the acidity of the solution. It should be noted that the by-products from the oxidation of the hydroxylamine hydrochloride are volatile NO_x compounds.

The final revolatilization of the mercury is accomplished by reducing the mercury with a stannous chloride solution. The half reactions are shown in Section 3 of Table 1. The stannous chloride will also reduce the nitric acid (used to acidify the permanganate) forming volatile NO_x compounds.

In this study 3% w/v aqueous permanganate solutions were prepared from reagent grade potassium permanganate and were filtered to remove any MnO_2 present in the original crystalline material. Acidic solutions (40 ml) were then prepared by adding concentrated nitric acid to achieve a 10% nitric acid concentration. Known concentrations of mercury in water (slightly acidified) were then added to these prior to analysis. A 10% hydroxylamine hydrochloride solution (5 ml) was used to reduce the excess permanganate and a 20% $SnCl_2$ in 50% HCl (3 ml) was used to reduce the bivalent mercury to elemental mercury. These solutions were then aerated, either directly through the spectrophotometer or amalgamated onto gold.

The acidification and reduction of the excess permanganate are both exothermic reactions. Optimization of the addition of the reducing agents showed that more $SnCl_2$ was required with the permanganate than with a mercury-water standard, even when the excess permanganate has been completely reduced. The results showed that 3 ml of the $SnCl_2$ solution was required compared to one ml with a similar mercury-water standard sample. (Additional hydroxylamine hydrochloride had no effect on the stannous chloride requirements.) This probably represents the reduction of the nitric acid which has a slightly higher oxidation potential than the elemental mercury (Table 1). NO_x compounds are released during both reduction steps. The final reduction of the mercury occurs in a closed system resulting in the inclusion of the volatile NO_x compounds in the sensing cell with the volatilized mercury, unless gold amalgamation (secondary amalgamation) is utilized. Several

investigators have suggested that NO_x compounds interfere with the analysis. Although some questionable results have been obtained, NO_x has not been correlated to problems with either the direct aeration or amalgamation procedures.

The reduced permanganate standards produced higher peaks than observed with water standards. The higher peaks are a result of the blank mercury concentration in the permanganate as well as a slightly quicker release of the mercury from the solution probably due to the excess stannous chloride.

Initial studies showed an increase in sensitivity with the age of the acidified permanganate. Approximately 3 hours was required after acidification before maximum sensitivity was obtained. More recent studies with both the 10% and 25% acidified permanganate samples showed no differences in sensitivities between samples stored for 15 minutes or 3 hours before analysis. Both series were performed by identical procedures and no explanations are offered for the observed differences.

MnO_2 is sometimes formed during the reduction of the excess permanganate. The brown precipitate disappears with additional stirring of the sample. The occurrence of the MnO_2 has not been correlated to any procedural differences and no analytical differences have been observed because of it. Mr. Joseph DeGarmo of American Electric Power has correlated this with deterioration of the magnesium perchlorate leading to absorption of the volatile mercury by the perchlorate.[6]

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[6]Personal Communication.

The stability of the spiked permanganate solutions reduced with hydroxylamine hydrochloride was investigated. Permanganate solutions spiked with 0.25 and 0.50 µg mercury were reduced with hydroxylamine hydrochloride and then stored for 10 min., 30 min., 1 hour, 4 hours, and 22 hours before final reduction and analysis. No significant differences were observed between the various intervals. It is the opinion of the authors that since the HNO_3 is not reduced by the hydroxylamine hydrochloride there should not be a significant loss of mercury with storage. This is in contrast to the results reported by Mr. S.T. Hirozawa of the Wyandotte Chemicals Corporation.[7]

Although some problems have occurred with permanganate solutions, the authors feel that when collecting inorganic mercury, accurate, reliable data can be obtained from permanganate solutions utilizing either direct aeration or amalgamation. The purpose of the oxidizing solutions in the stack sampling procedure is to split or dilute the sample. This will decrease any peculiar effects of the solution.

b. ICl

The ICl method utilized in this study was the Determination of Mercury in Particulate and Gaseous Emissions from Stationary Sources developed by EPA.[8] The results obtained from this procedure are presented in

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[7] S.T. Hirozawa and J.M. Rottschafer, "Trip Report - Mercury Emission Via Hydrogen Gas and Fume Headers at Port Edwards," memo to C.V. Francis, 1/15/71.

[8] Federal Register 36(234), Dec. 7, 1971

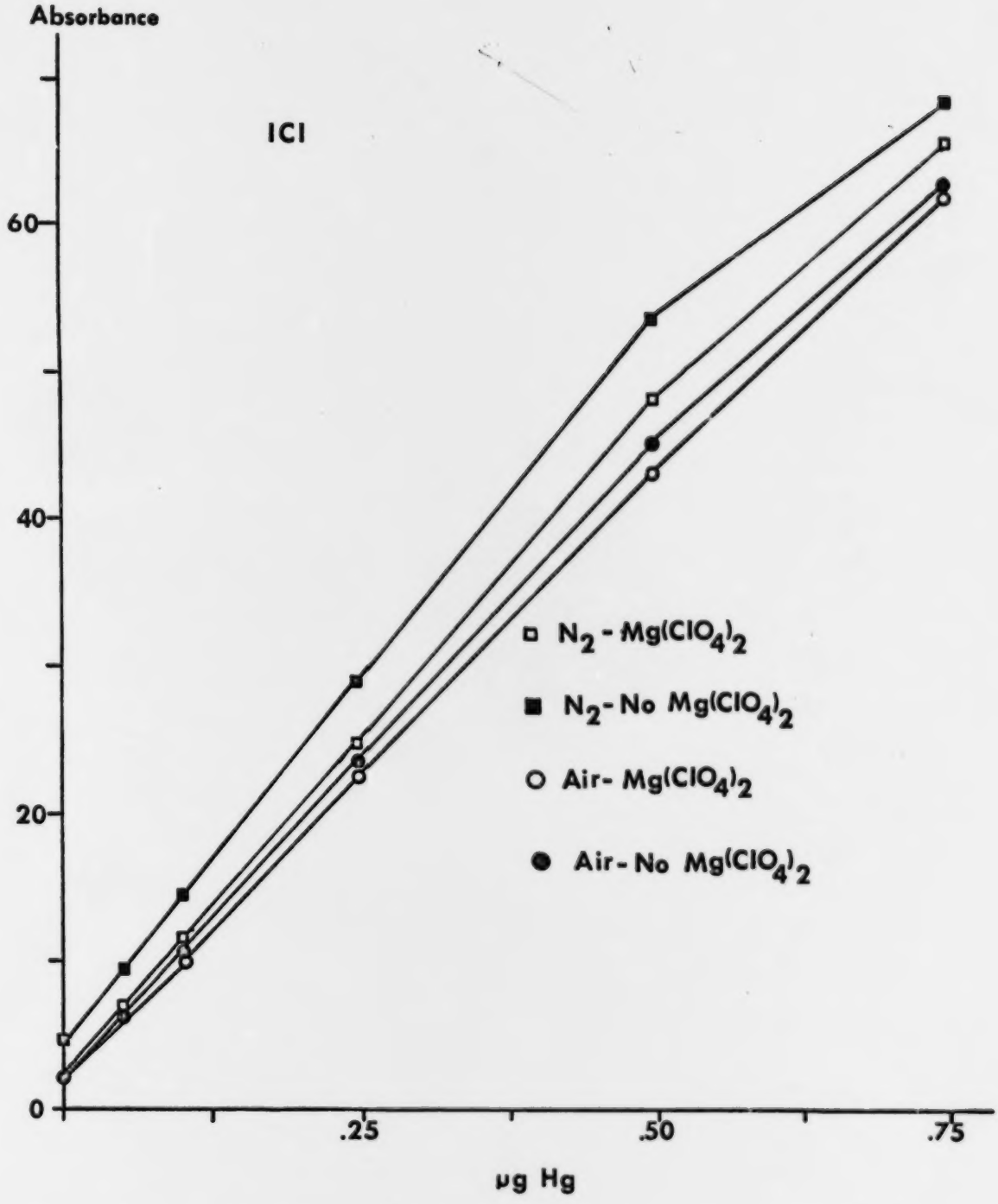

Figure 5. Analytical Curves obtained from Direct Aeration of ICl Standard Solutions.

Figure 5. The technique is extremely sensitive to any procedural variations and the presence of any water or water vapor in the system. This resulted in extensive practice being required for each technician involved in the study. Even with experienced personnel different individuals could not obtain acceptable agreement in results. Because of this, the utilization of this procedure for routine analyses is questioned by the authors.

4- Water Background

Water vapor will absorb 254 nm radiation resulting in erroneous peak heights when determining mercury concentrations. This interference is dependent upon the relative humidity and may be eliminated by utilization of the gold amalgamation technique or a desicant, such as magnesium perchlorate, between the aeration cell and the optical cell. The amalgamation procedure separates the water vapor and the mercury by collecting the mercury on the gold and passing the water vapor. With the direct aeration procedure the water vapor is eliminated by absorption onto magnesium perchlorate.

Figure 6 illustrates the effect of utilizing magnesium perchlorate with the direct aeration technique under high humidity conditions. These results were obtained under high humidity conditions using nitrogen as the carrier gas. Under dry humidity conditions, essentially no background water vapor is observed when using the direct aeration technique. Extensive analyses of these parameters has shown that a high background water vapor value is obtained under high humidity, even when the air or

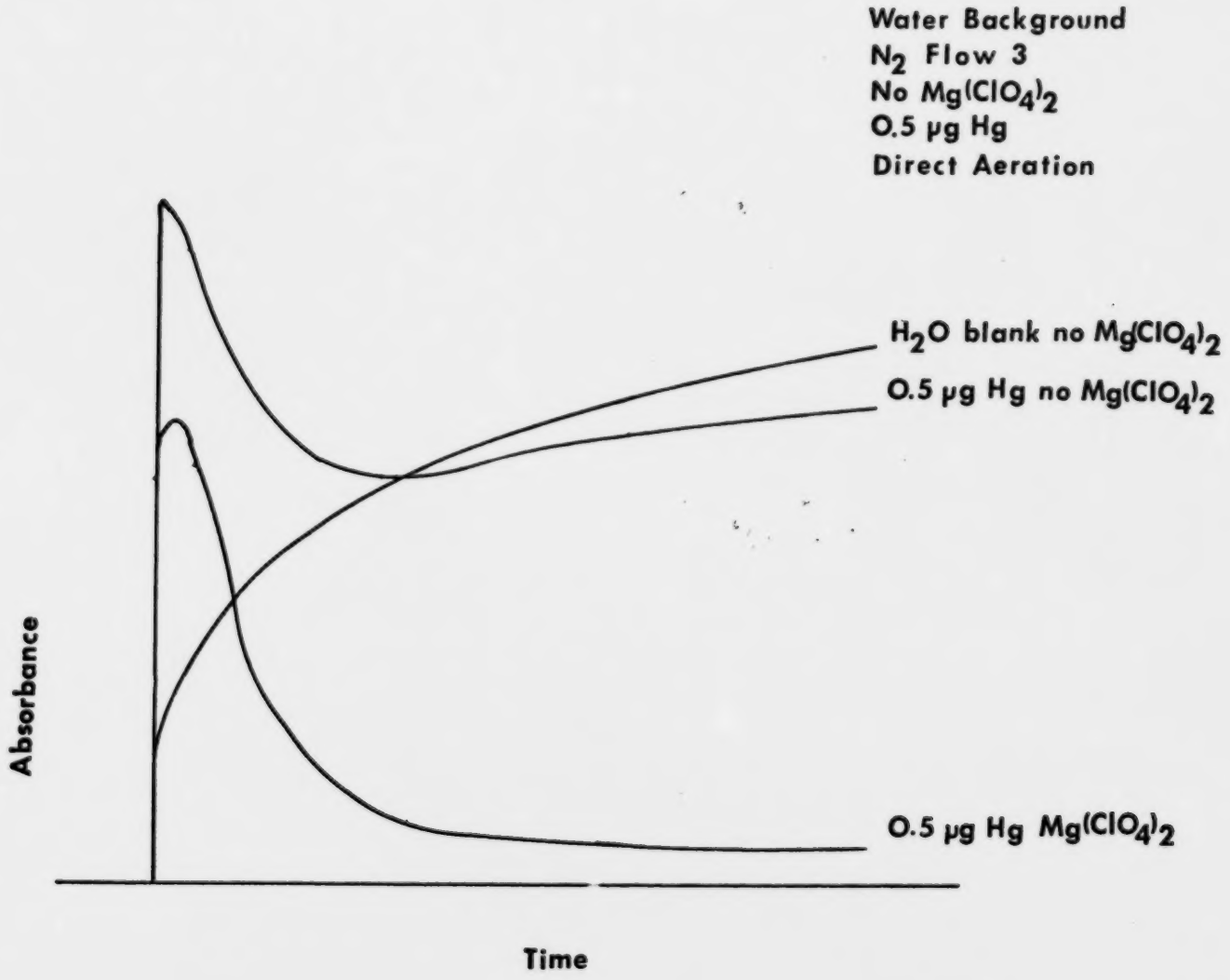

Figure 6. Effect of Magnesium Perchlorate on Water Absorption under High Humidity Conditions.

nitrogen used as the carrier gas is dried before the aeration cell. Since the air in the dead space above the liquid phase in the aeration cell is quickly purged with the carrier gas, it is concluded that high humidity conditions have a chemical effect on the liquid sample resulting in the vaporization of more water under these circumstances.

With the introduction of magnesium perchlorate as a desiccant between the aeration cell and the optical cell this background is eliminated (see Figure 6). Magnesium perchlorate has been observed by the authors and reported by other investigators to undergo deterioration and eventually absorb the volatile mercury. To determine the effect of this deterioration in order to know when the magnesium perchlorate should be replaced, water was added dropwise to the magnesium perchlorate and standard analytical curves were obtained. The results of this study are shown in Figure 7. There were no significant losses of mercury observed. Additional water was added until it had completely saturated the magnesium perchlorate. There was no loss of mercury until the tubing below the desiccant became clogged with the saturated suspension. Temperature effects have been observed to deteriorate the magnesium perchlorate resulting in the absorption of mercury. If, when using the secondary amalgamation technique, magnesium perchlorate is positioned between the amalgamator and the optical cell, a significant loss of volatile mercury is observed after the first few runs. Apparently, this is related to the effect of the hot air, obtained when the amalgam is fired in the induction furnace, interacting with the magnesium perchlorate.

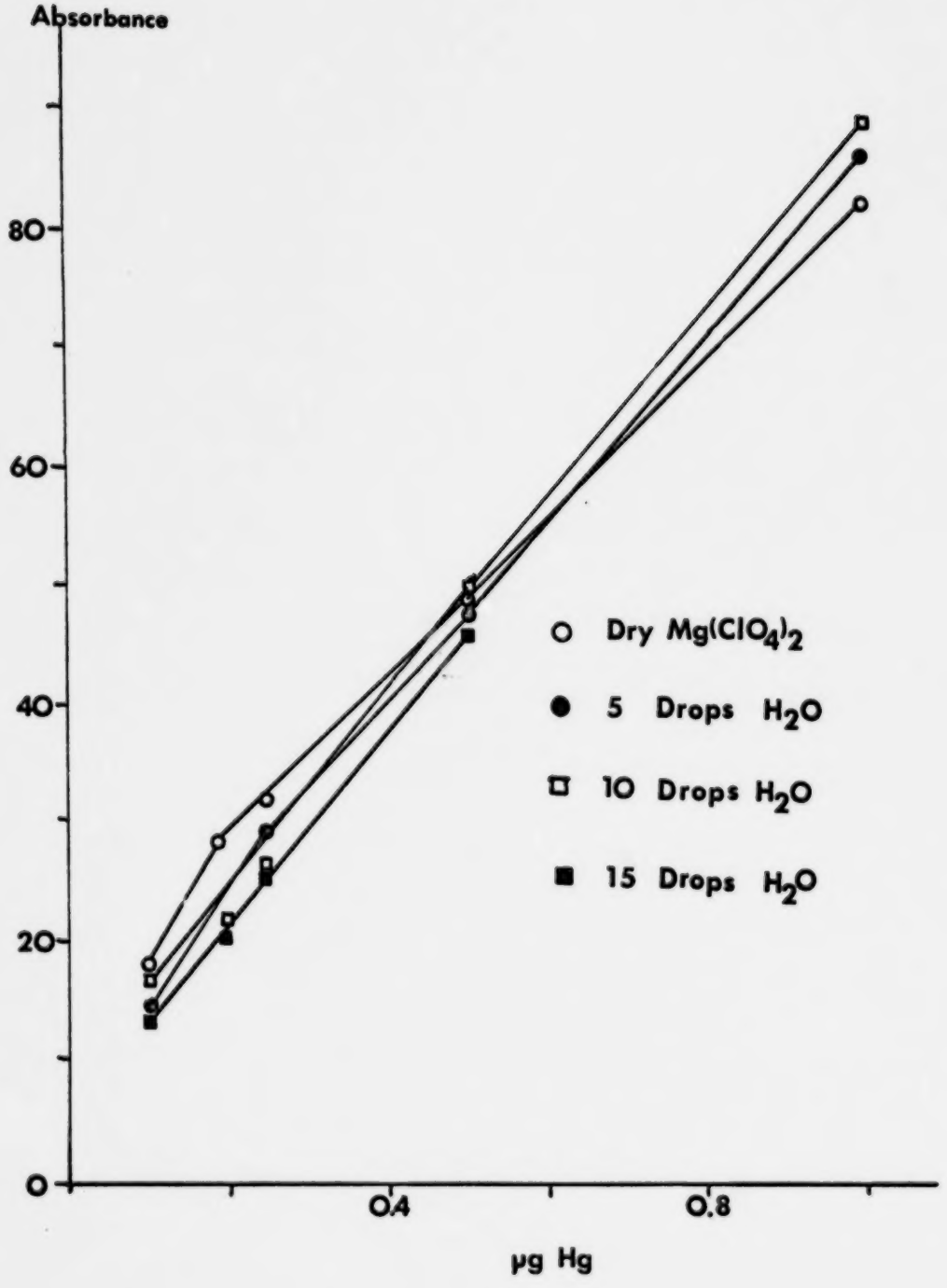

Figure 7. Analytical Curves obtained by Direct Aeration illustrating the Effect of Water on Magnesium Perchlorate Deterioration.

Without magnesium perchlorate the observed water background is related to the temperature of the aqueous solution to be aerated as well as the relative humidity. Figure 8 illustrates this relationship. This relationship is critical when a potassium permanganate solution is used since the reduction with the hydroxylamine hydrochloride and the stannous chloride is exothermic.

5- Carrier Gases

Compressed air and nitrogen were investigated as possible carrier gases in the system. With the use of magnesium perchlorate there were no differences observed between the two gases. Figure 9 contains the analytical curves obtained with magnesium perchlorate with $KMnO_4$ and H_2O standards using both nitrogen and air as the carrier gases. Without magnesium perchlorate, compressed air volatilized more water than nitrogen, resulting in a higher water vapor background.

6- Direct Aeration

Figure 10 illustrates the differences observed in the standard curves obtained by direct aeration from $KMnO_4$, ICl and H_2O standard solutions. The $KMnO_4$ curve shows the blank mercury concentration as would be expected. The parallel lines of the $KMnO_4$ and H_2O standard curves show that the rate of release of the mercury from the two solutions is very similar. The different slope of the ICl curve illustrates a slightly different rate of release of the mercury. This partially explains the lower curve obtained with ICl, but it still appears that not all the mercury is being released during the reduction and aeration.

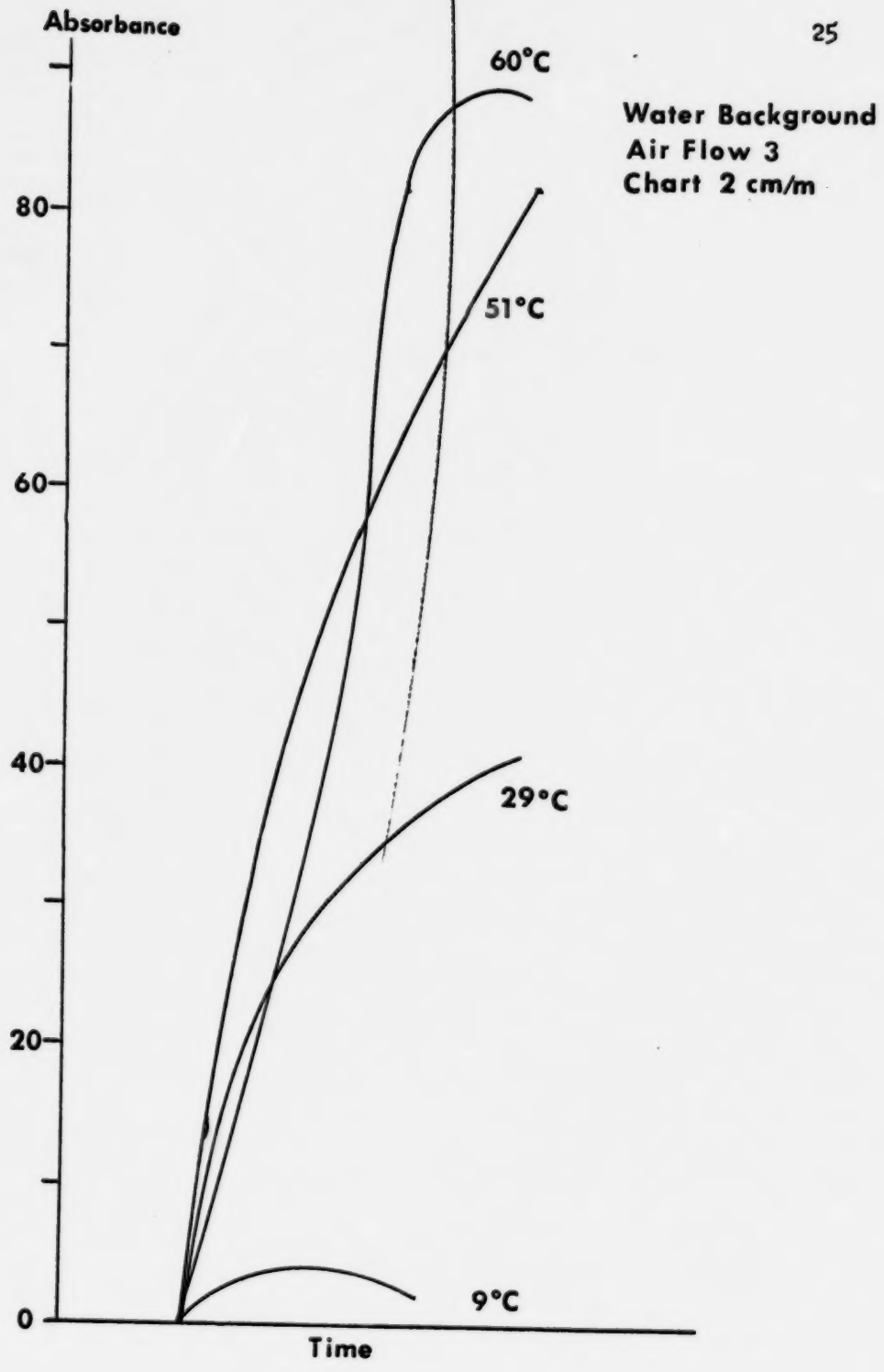

Figure 8. Water Absorption at 254 nm as a Function of Water Temperature.

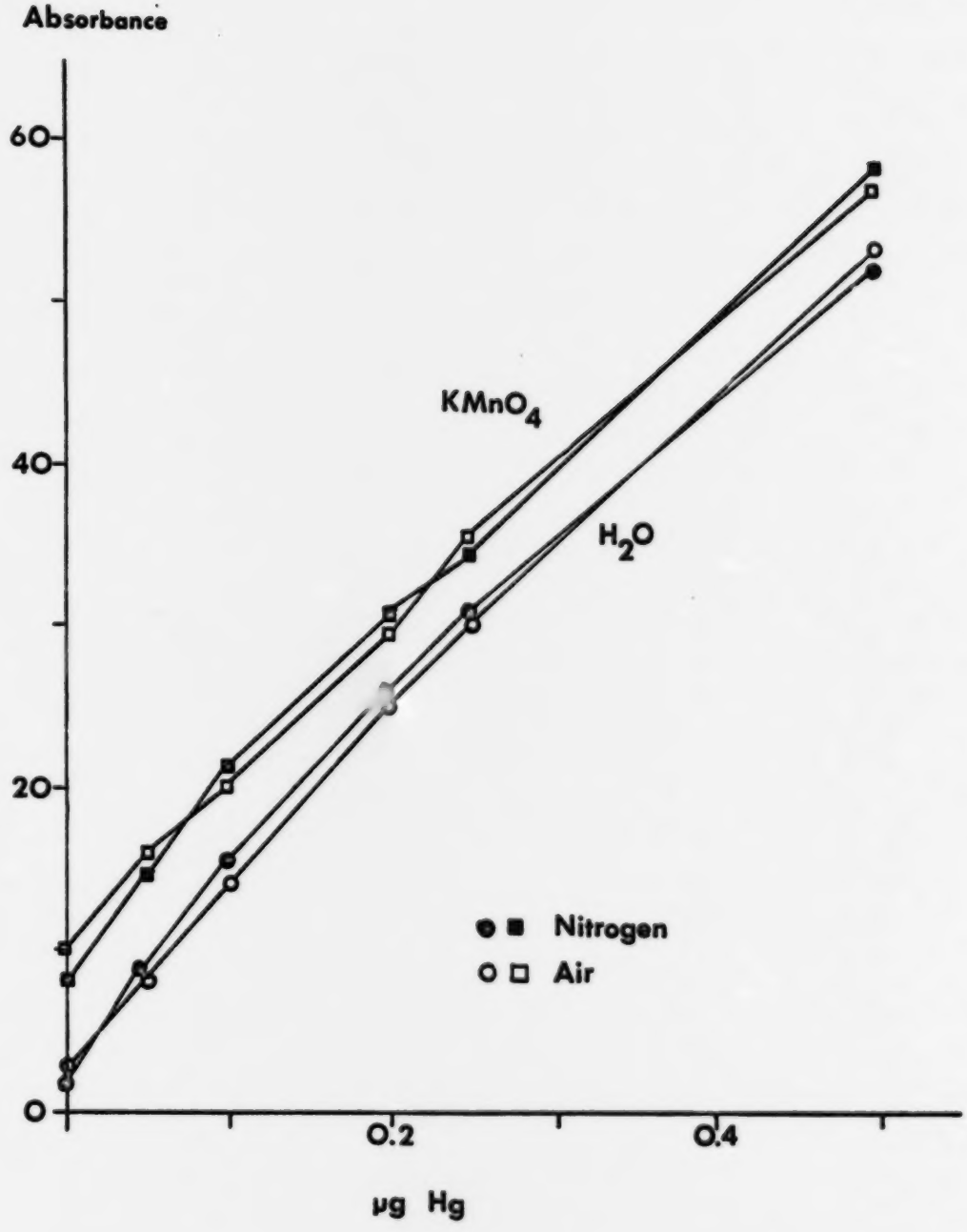

Figure 9. Analytical Curves obtained by Direct Aeration utilizing Magnesium Perchlorate with $KMnO_4$ and H_2O Standard Solutions and Nitrogen and Air as the Carrier Gases.

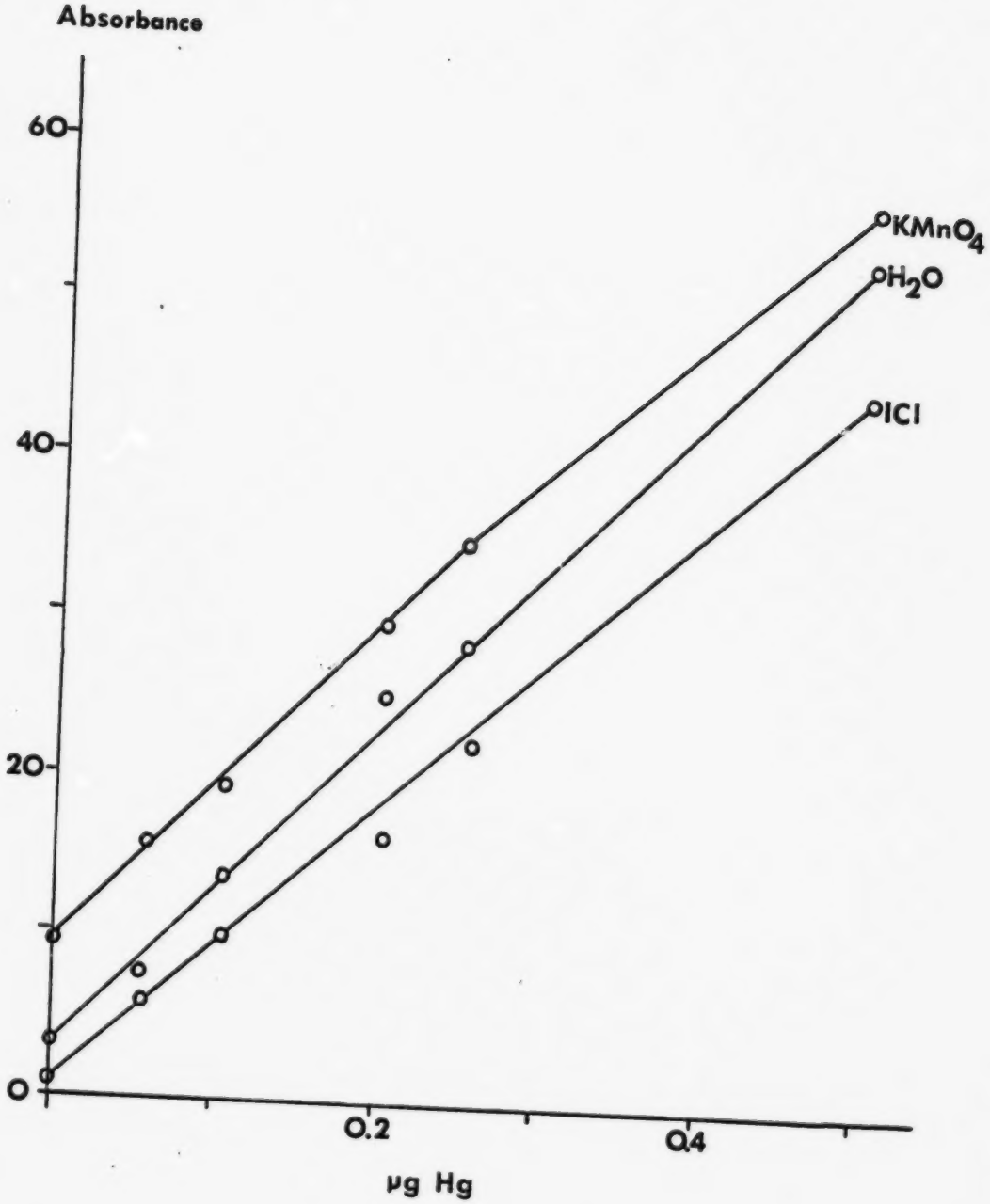

Figure 10. Analytical Curves obtained by Direct Aeration of $KMnO_4$, ICl, and H_2O Standard Solutions.

The difficulties with the reproducibility of the analytical results using ICl and the slower release rate of the mercury from the ICl solution results in the recommendation to adopt the $KMnO_4$ solution when studying volatile elemental mercury as it is observed in smelters.

7- Amalgamation

Figure 11 illustrates the results obtained from amalgamating mercury aerated from $KMnO_4$ and water standard solutions. The blank mercury concentrations are similar to those observed with direct aeration from permanganate solutions. The amalgamation procedure, firing the gold-mercury amalgam in a Leco induction furnace at a 90% variac setting in conjunction with an LDC Mercury Monitor (range 0.64), results in an absorbance of 70 with a 0.2 μg sample of mercury. As discussed previously, this is extremely sensitive and greatly limits the working range of the procedure.

8- Recommended Analytical Procedure

The laboratory study has resulted in the adoption of the direct aeration procedure in conjunction with $KMnO_4$ solutions. Compressed air or nitrogen may be used as the carrier gas. It is recommended that a magnesium perchlorate drying tube be incorporated into the system. Either the LDC Mercury Monitor or a standard atomic absorption spectrophotometer may be used. The analyses of the samples collected in the field portion of this study utilized compressed air as the carrier gas and an LDC Mercury Monitor. The final recommended analytical procedure is presented in Appendix II.

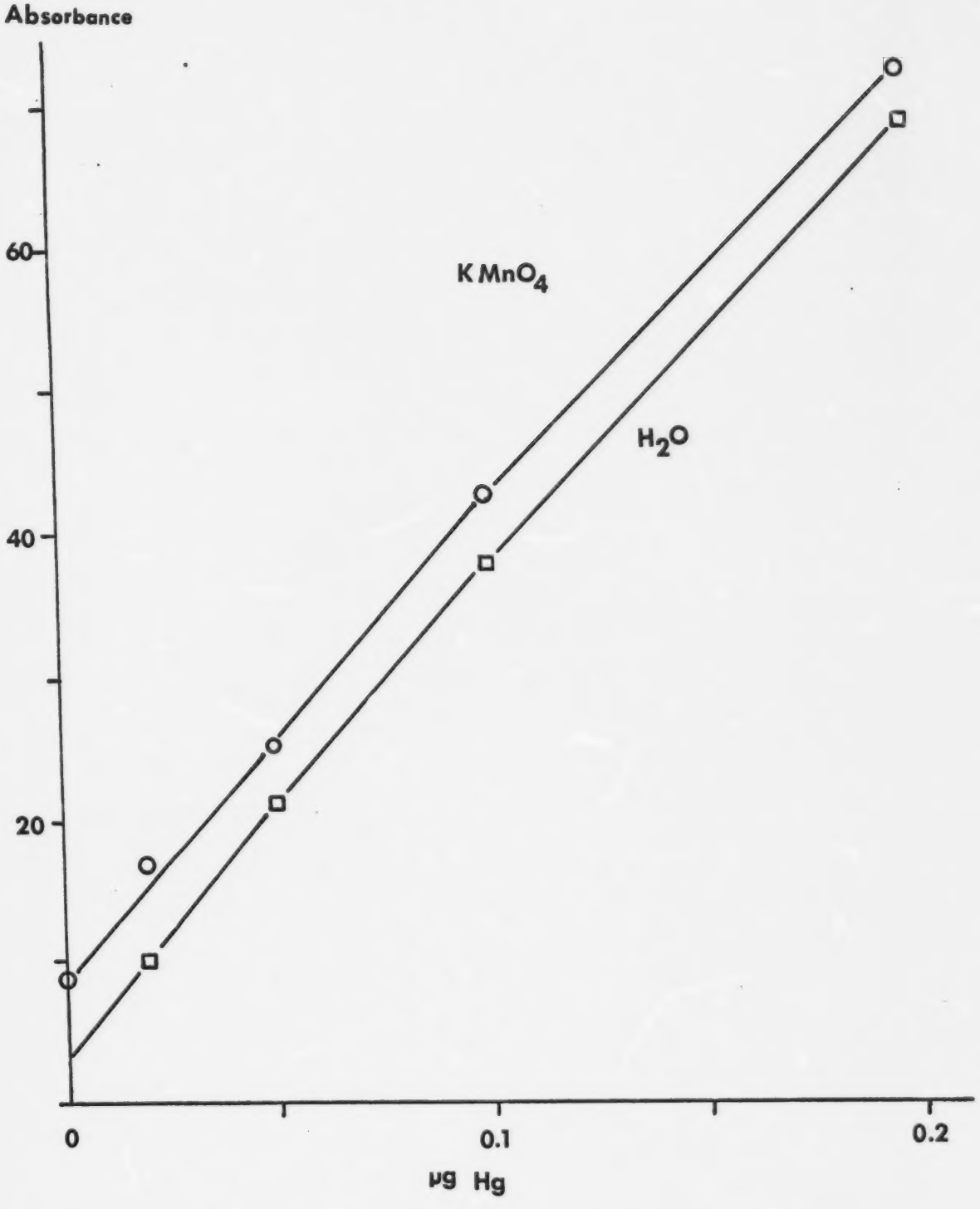

Figure 11. Analytical Curves obtained from $KMnO_4$ and H_2O Standard Mercury Solutions by Amalgamation.

9- Mercury Capacity of the Gold

The efficiency of mercury retention by the gold in the amalgamators was determined by measuring the amount of mercury bypassing the gold. This was studied in the laboratory by reducing and volatilizing a standard mercury solution which was carried by an air stream (1.4 liters/minute) through a gold amalgamator. The mercury bypassing the amalgamator was absorbed in a $KMnO_4$ solution using the bubbler assembly. This solution was then analyzed by the direct aeration method. Determinations were obtained from solutions containing quantities of mercury up to 70 µg. The results of this study utilizing a standard 15 mm diameter amalgamator are illustrated in Figure 12. 25 mm diameter amalgamators (shorter height of gold) showed a greater bypass of mercury than the 15 mm amalgamators with comparable amounts of gold. The results of this study are dependent upon the air flow rate and thus does not represent a true maximum mercury capacity of the gold. (Since amalgamation represents the mercury dissolving the gold at the point of contact there is no ultimate mercury capacity of the gold.) The results of this study are used to obtain a rough indication of the amount of gold required when obtaining a stack gas sample.

10- Filter Analysis

The filters obtained during the isokinetic sampling of stack gases must be analyzed for mercury to determine the total mercury concentration of the gas stream. Two analytical methods for dissolving the particulates were investigated:

(1) One half of the filter was boiled in 10 ml of concentrated

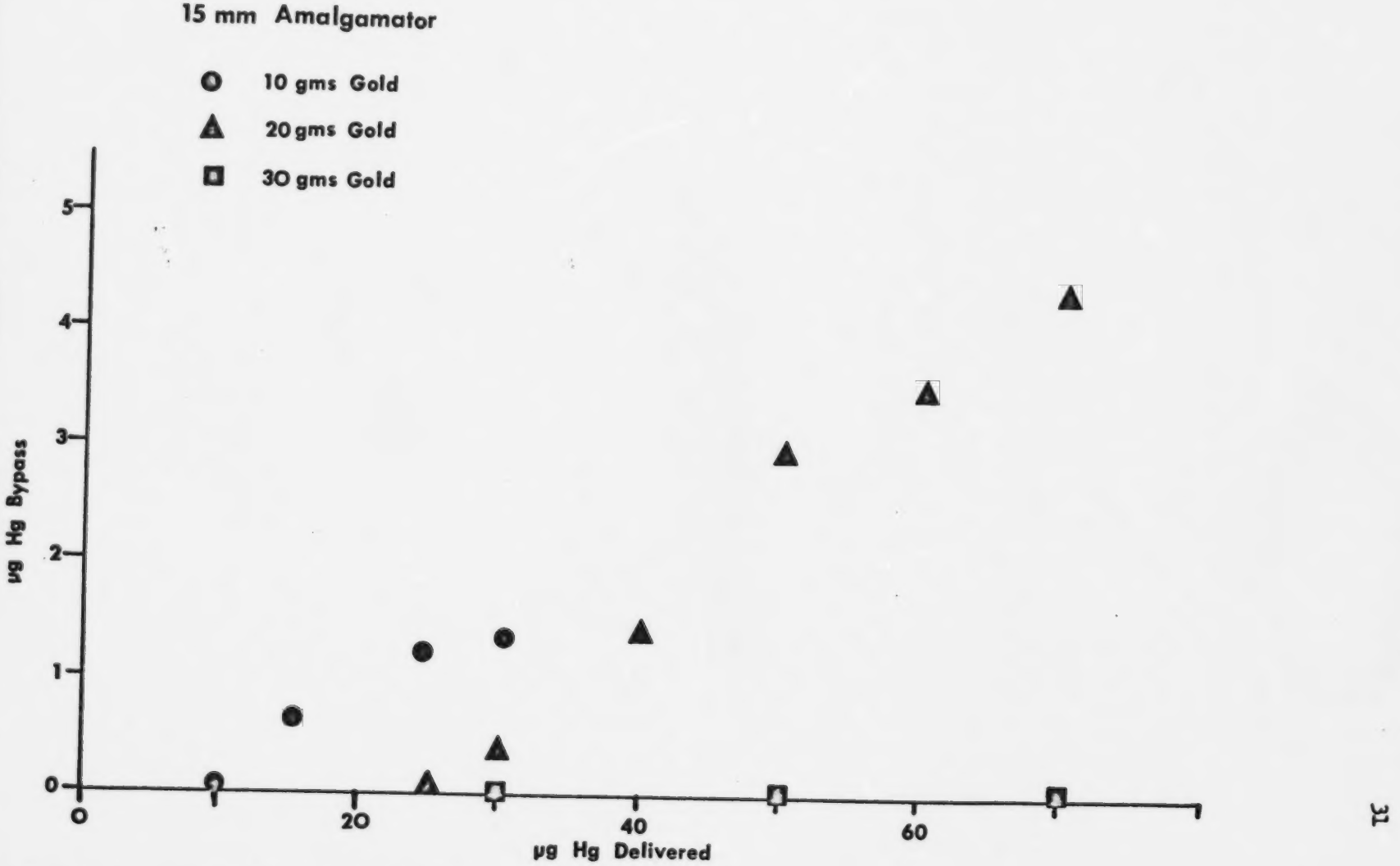

Figure 12. Mercury Collection Efficiency of Gold Amalgamators: Mercury Bypass as a Function of the Quantity of Gold.

nitric acid for 10 minutes. The filter was disintegrated with a high pressure stream of distilled water and the mixture was diluted to 100 ml.

(2) The other half of the filter was placed in a Bethge apparatus with 2 mg ammonium meta-vanadate (catalyst), 5 ml nitric acid, and 10 ml 70% perchloric acid. The mixture was heated, collecting and withdrawing the nitric acid. The filter was then digested in the refluxing perchloric acid for 10 minutes. The nitric and perchloric acid solutions were combined and diluted to 100 ml.[9]

After cooling, the solutions were analyzed for mercury by placing 50 ml aliquots in the interchangeable sample holders, reducing the mercury with 2 ml of the stannous chloride solution and aerating the mercury through the LDC Mercury Monitor at a flow rate of 1.4 liters per minute.

Both methods dissolved all visible particulates and produced comparable data within experimental error. Because of the simplicity of the procedure, the nitric acid method is recommended and was used by this laboratory for the field phase of this study.

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[9] "The Wet Chemical Oxidation of Organic Compositions Employing Perchloric Acid." The G. Frederick Smith Chemical Co., Inc., 1965.

FIELD INVESTIGATIONS

1- The Sampling Site

The samples for this study were taken at the American Smelting and Refining Company (ASARCO) zinc smelter in Columbus, Ohio. A flow chart of the initial smelting process at this plant is given in Figure 13. The ore is roasted at 900°C in a fluid bed roaster volatilizing the sulfur as SO_2, and the mercury, presumably, as elemental mercury (the high temperature of the roasting operation and the fact that there is essentially no organic material present in the ore precludes the formation of volatile organo-mercury compounds). The particulates are removed from the gas stream by a waste heat boiler, a cyclone and two electrostatic precipitators and the gas is then carried through a 3.5 foot diameter horizontal steel pipe (the cross-over duct) running about 60 feet above ground level to the acid recovery plant, where the SO_2 is converted to sulfuric acid. This duct has a 150 foot straight section, without constriction or bends, and a single 4-inch sampling port was located in this duct about 30 feet from the down-stream end. The flow in this duct is controlled by ID and FD fans, resulting in a positive-negative pressure interface which migrates back and forth along the duct in the area of the sampling port. Under normal running conditions, static pressure at the port was usually within $\pm$ 0.5 inches of water.

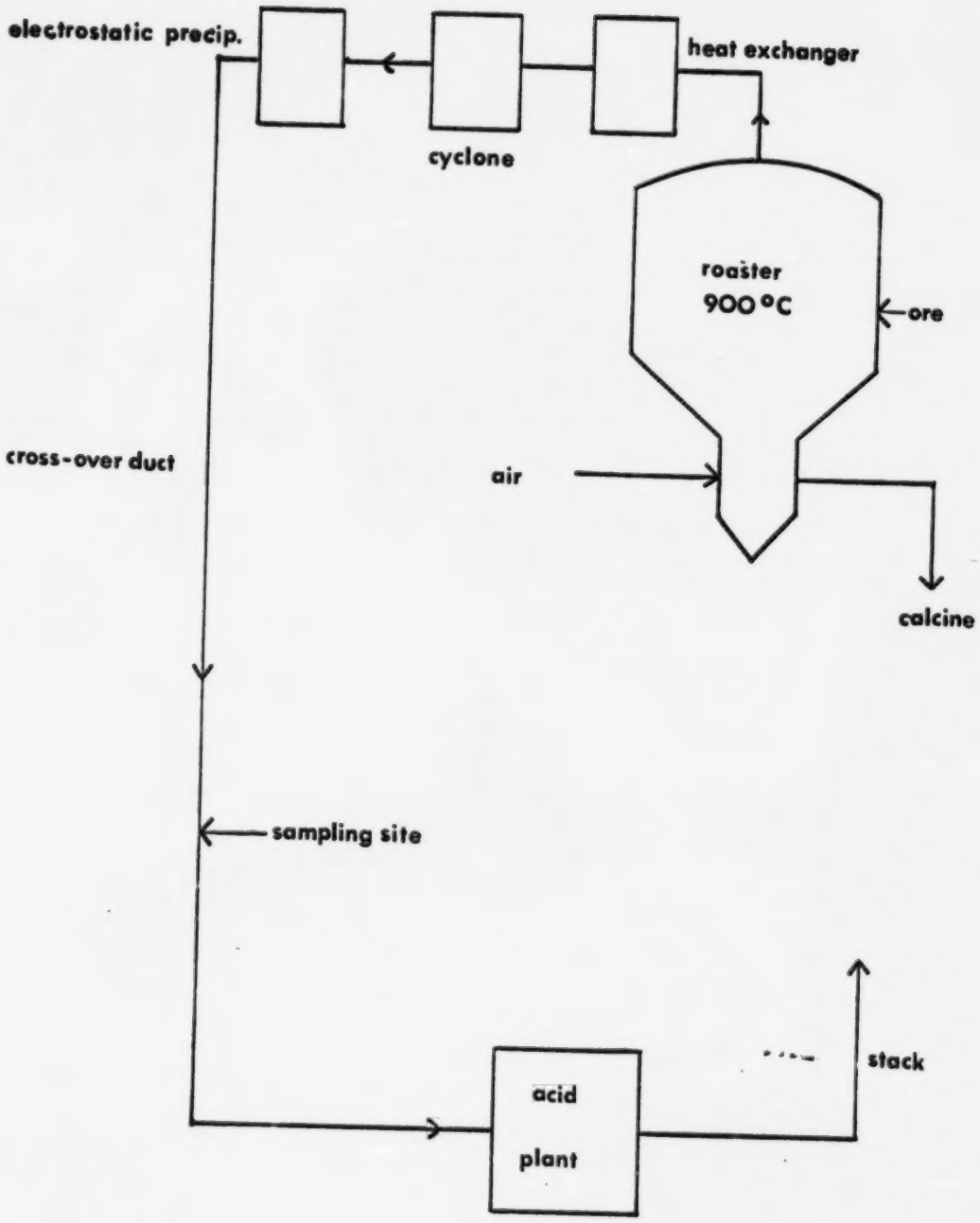

Figure 13. Flow Chart of the Initial Smelting Process at the ASARCO Columbus, Ohio Zinc Smelter.

The gas stream in the duct contains about 7 - 8% SO_2 and flows at a rate of 12,000 - 15,000 CFM. The average molecular weight of the gas has been calculated to be 31.4 and contains about 5% water (figures provided by ASARCO and EPA).

2- Sampling Equipment

The samples for this study were taken with a standard Model 2343 RAC "Staksampler" portable stack gas sampling unit utilizing a 5-foot glass probe heated to 150°F. The sampling train was a standard EPA isokinetic sampling train with some of the wet impingers replaced by amalgamators. It consisted of a probe mounted on a sample box and connected to a cyclone and filter which were enclosed in a heated compartment, then a series of impingers (and/or amalgamators) in an ice bath, followed by an impinger containing silica gel. The sample box was connected to the console containing the dry gas meter and pump by a 30-foot umbilical cord.

Modified Greenburg-Smith impingers (without the tip) were altered as shown in Figure 14 by forming three indentations in the center (to support a quartz wool plug and the gold) and attaching a 28/15 pyrex ball joint to the bottom of the straight vertical tube. These units, called amalgamators, can be inserted into a standard EPA isokinetic sampling train in place of the standard impingers. The interchangeability of impingers and amalgamators permits the use of a combination of amalgamation and wet absorption techniques to verify the collection efficiency of the various components. This style of amalgamator also

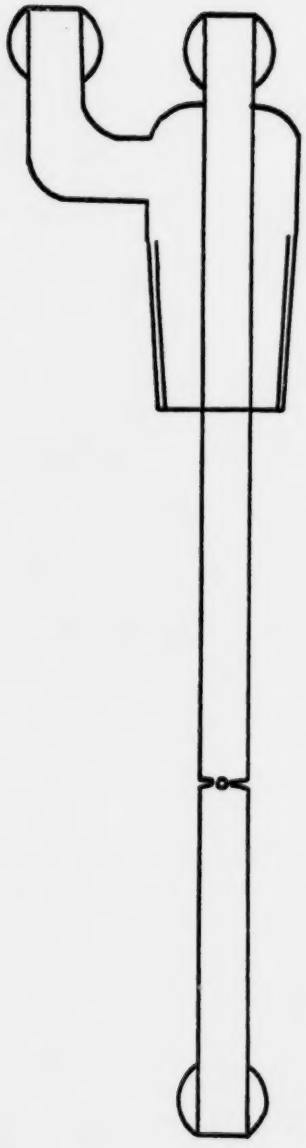

Figure 14. Illustration of the 15 mm Amalgamator.

allows the standard isokinetic sampling train to be used for collection of mercury without major alterations to the equipment.

For the purpose of this study, a larger number of impingers/amalgamators were used in the sampling train than are ordinarily employed for isokinetic sampling. The sampling box was originally designed to hold 4 impingers in the ice bath, including the silica gel. For this work, as many as nine impingers (including the silica gel) were used in the sampling train. A maximum of six could normally be placed in the sample box, and two more could be taped to the outside of the box. By compressing the insulation somewhat on one of the two sample boxes used, it was possible to fit seven impingers inside the box and two more could be taped to the outside. As a result the box was severely crowded and some misalignment of the connecting tubes was unavoidable. In addition, some of the cooling capacity reserve of the box was lost as there was less room for the ice/water mixture and the impingers touching the inside edge of the box were not surrounded on all sides by the coolant.

Since the ambient temperature during this work was fairly low (mostly in the 30's) and the runs were comparatively short (5 - 15 minutes), no troubles were experienced keeping the impingers well cooled. It was observed, however, that when the ambient temperature rose occasionally to the 40's or 50's, the ice was somewhat depleted after about 10 to 15 minutes running time.

During this work, a considerable quantity of SO_2 was drawn through the

console unit. In this procedure, the SO_2 is not removed at the sample box but continues through the pump and dry gas meter. After each run about 1 CF of ambient air was drawn slowly through the intake of the silica gel impinger in an effort to rinse out some of the SO_2 in the console unit. Some difficulty was experienced with the pumps in the consoles. The pumps were periodically found to pull erratically or not at all. Disassembly of the pump according to instructions furnished by the manufacturer showed that the oil which normally lubricates the sliding fiber vanes had congealed so that the vanes were sticking in their slots in the rotor. The pumps were cleaned with solvent (acetone) and reassembled. The oil in the reservoir was changed to a mixture of 75% SAE 10 and 25% kerosene as recommended by the manufacturer for operation at temperatures below freezing. After this treatment, the pumps ran smoothly for two or three runs and then started to operate erratically as before. It was then necessary to disassemble and clean the pumps again. A similar difficulty was experienced with the check valve in the metal adapter which goes from the last impinger to the umbilical cord. Toward the end of this work the check valve on both adapters became corroded and stuck in a partially closed position, causing a high flow resistance at that point. The check valve assembly was removed from the adapter.

3- Field Sampling Procedure

Since glassware stored openly in the laboratory may absorb traces of

mercury,[10] all glassware was rinsed before use with the sequence: 1% $SnCl_2$ in 2.5% HCl, 1:3 HNO_3-H_2O, distilled water, acetone, and then dried.

The amalgamators were prepared for each run as follows. A small plug of quartz wool was inserted from the top and pushed into place against the supporting indentations. A length of ¼-inch dowel rod and a stiff (about #10) wire are handy to help wedge the wool into position. In earlier work, the authors used a small wad of gold wire for this purpose, which sometimes became loose in the tube from handling and allowed some of the finer gold particles to fall out the bottom of the tube. No trouble of this sort was ever encountered with the quartz wool plug. The gold chips were prepared by cutting up a 0.007-inch thick sheet of the metal into small 1/16-inch squares. These gold chips were placed in small crucibles and fired overnight in a refractory oven at about 600-700°C. At the start of each day's sampling, the gold was removed from the oven and allowed to cool. The gold chips were then weighed out and poured into the amalgamator on top of the plug, using a plastic funnel. The amalgamator was held in a vertical position and tapped gently to help settle the chips. The amalgamator was then fired in the induction furnace to insure that any

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[10] J.D. Brooks and W.E. Wolfram, American Laboratory 3(54), (1971).

mercury picked up during the handling procedure from glassware, plug, etc., was driven off before the amalgamator was assembled into the train. The train sequence was then assembled for each run as shown in Part B of Appendix II.[11]

After positioning the sample box at the port, the heater was turned on, the ice compartment filled with ice and water and a leak check was performed. The probe was then connected and inserted with the tip facing upstream (with the exceptions of Runs 61 and 62 where the tip was positioned facing downstream). The 0.25-inch diameter tip was used for Runs 1 - 60 and 71 - 72; the 0.50-inch diameter tip was used for Runs 61 - 70. After the probe and sample box had been allowed to come to the proper temperature (probe heater setting was 100% (150°F); sample box 250°F), the pump was turned on and the flow adjusted to give the desired sampling rate. A stopwatch was used to time the run. In a five-minute run the dry gas temperature, stack temperature, etc., were read at 2-½ minutes. On longer runs the readings were made every five minutes.

After obtaining the sample, the probe and sample box were taken to the on-site mobile laboratory for the cleanup procedure. Wide-mouthed jars, holding a pint or six ounces and equipped with plastic caps and liners were used to store the samples for transport to the laboratory. These jars were cleaned before use with the rinse sequence described above.

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[11] See the explanation of the Data Table given on page 45.

A stock solution of 3% $KMnO_4$ in 10% HNO_3 was freshly prepared every other day. This acidic permanganate was used to stabilize the mercury in the samples taken from the train.[12]

The following cleanup procedure was adopted to account for all mercury deposited in any part of the train ahead of the silica gel. Distilled water was used for all rinses unless otherwise noted.

1. The probe, cyclone, and the glass parts of the filter assembly were washed into a 1-pint jar containing 25 ml of the 3% $KMnO_4$ solution. The total volume of this solution was measured in the laboratory prior to analysis.

2. The filter (previously weighed) was placed in a disposable plastic petri dish and marked with the run number.

3. The inside portion of the first impinger (A position) and the right angle connector leading into it were rinsed into the contents of the impinger "shell". When this impinger had originally contained distilled water, $KMnO_4$ was added to oxidize the SO_2 and mercury in solution. This was found to be necessary after initial attempts to analyze the SO_2 saturated water for mercury gave highly erratic results from the evolution of SO_2 when the mercury was aerated after reduction. The volume of this solution was measured with a graduate and it was transferred to a one-pint bottle.

4. Each "empty" impinger in the train (and the connector leading to it) was rinsed into a six-ounce jar containing 25 ml of the $KMnO_4$ solution. The total volume of this rinse was measured and recorded. This step was found to be necessary when it was discovered that moisture condensed in an empty impinger often contained appreciable amounts of mercury, particularly if that impinger was ahead of the first amalgamator.

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[12] R.V. Coyne and J.A. Collins, Anal. Chem. 44, p. 1093 (1972).

5. Each amalgamator case and its leading connector were rinsed into separate jars, each containing 25 ml of $KMnO_4$ solution as outlined in Step 4.

6. Each amalgamator was fired into 50 ml of the 3% $KMnO_4$ solution. The apparatus used for firing the amalgamators into permanganate is shown schematically in Figure 15. The lower portion of the bubbler consists of a closed tube of about 100 ml capacity with a standard taper fitting which matches a female taper on the body of the bubbler assembly. These tubes were used as interchangeable sample holders for the $KMnO_4$ solutions. The amalgamator was centered in the coil of the induction furnace and connected to the nitrogen supply and the bubbler with two female ball-joint adapters and two clamps. The nitrogen flow was set at 0.5 liters per minute. The induction furnace was equipped with a variac to control the energy transmitted to the coil. Firing was commenced at a setting of 60% and increased 5% each minute until the gold was glowing. This was done to avoid a large "spike" of mercury into the bubbler, and to insure complete firing of the gold. Laboratory tests on mercury aerated from aqueous solutions into 40 ml of 3% $KMnO_4$ showed no bypass of the permanganate for 100 µg of mercury aerated at an air-flow rate of one liter per minute. After the firing of each amalgamator, the sample tube was detached, the drops of permanganate clinging to the bubbler tube were rinsed into it and then the contents of the tube was rinsed quantitatively into a properly labelled six-ounce wide-mouthed jar. The amalgamators were fired in reverse order (i.e., A_5, A_4, A_3, A_2, A_1) to minimize contamination of successive samples by drop carry-over. After firing, the amalgamators were assembled into the train to be used for the next run of the day. After the series of amalgamators had been fired, the bubbler apparatus and all of the sample tubes were cleaned, using the rinse procedure described above. It was found necessary to replace the tygon tubing connecting the amalgamator to the bubbler for each run in order to avoid contamination of succeeding samples by mercury adsorbed and then desorbed by the tygon. This tygon tubing was kept short (2-½ inches) to minimize mercury loss.

Upon receipt in the laboratory, each sample (from an amalgamator) was diluted to 100 ml in a volumetric flask just prior to analysis.

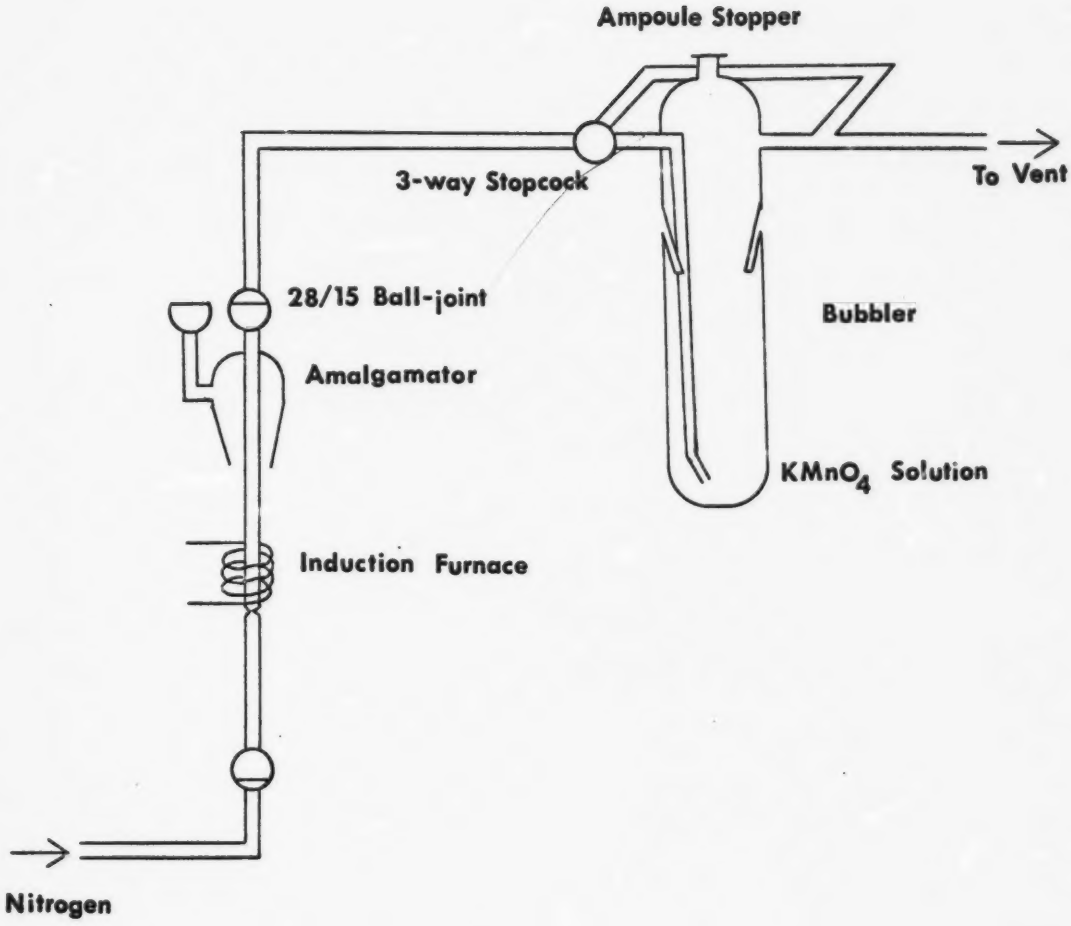

Figure 15. Apparatus used for Firing the Amalgamators.

7. The volume(s) of the $KMnO_4$ backup solution(s) (where these were used to back up the gold train) was measured with a graduate and the solution was transferred to a one-pint jar. Any permanganate stain remaining on the impinger was removed with a few drops of 10% hydroxylamine hydrochloride followed by a rinse with distilled water. The volume of these rinsings was measured and they were added to the permanganate in the sample jar.

8. A 50 ml blank of the permanganate solution was taken each day, placed in a six-ounce jar, and sent to the laboratory with the samples.

A field record was kept of all data recorded during the run and of each sample taken for analysis from the train. At the end of each day the sample jars were packed in cartons and transported to the laboratory for analysis.

4- Laboratory Analytical Procedure

Upon receipt of the samples by the laboratory, the volume of the probe and cyclone washings were measured and recorded along with the total volume of each of the other solutions, with the exception of those obtained from firing the amalgamators. The latter were each diluted to 100 ml in a volumetric flask. A suitable aliquot of each of these samples was then withdrawn by pipette and analyzed for mercury by the direct aeration procedure. The filters were analyzed by digestion with nitric acid, followed by analysis using the direct aeration technique. The procedures used are those developed under "Laboratory Investigations" and are described in detail in Appendix II.

RESULTS AND DISCUSSION

1- The Data Table

The data for each of the samples taken during this study is listed in Appendix I. Because of the large number of items associated with each run, the table is divided into Parts A and B on separate pages. In general, Part A contains the data taken in the field and Part B contains the data resulting from the laboratory analysis of the samples. Where there is more than one entry for a run in a column of Part A, the entry represents data taken every five minutes of a 10- or 15-minute run. In Part B, under the general heading of "Train Configuration" there are four horizontal lines of data across Columns A through H. The letter of the column heading represents the position of the impinger or amalgamator in the train sequence, counting from the filter (position "A" is the one immediately following the filter, "B" is next, etc.).

The topmost of the four horizontal data lines for each run is a code describing the contents of the impinger or amalgamator in that position:

H = Distilled water, 250 ml

E = Empty impinger

A = 20 grams of gold chips in each amalgamator of the series unless another amount is indicated.

K = 250 ml of saturated $KMnO_4$ solution unless some other quantity is indicated.

S = 250 ml 1% $SnCl_2$ in 2-½% HCl

HS = 250 ml distilled water used for the run, then 13 ml 20% $SnCl_2$ in 50% HCl were added to the impinger and ambient air drawn through at that point for about 3-5 minutes in an attempt to aerate the mercury in that impinger onto the following amalgamator.

The second of the four horizontal lines for each run gives the total number of micrograms of mercury found in that impinger or amalgamator. Under this is given in parentheses the micrograms of mercury found in the amalgamator case and connector washings. On the fourth line the distribution of mercury among the amalgamators is given on a percentage basis. This figure is useful for comparison of the performances of the amalgamator trains used in the various runs.

Under the column headed "Total Hg", the total mercury found in the entire train is given. Under this value is listed the percentage of that total found in all parts of the train except the permanganate backup solution. This gives a figure which corresponds to an experimentally determined percentage of total mercury recovery for the system, as it would be used for longer runs, without $KMnO_4$ backups. It also gives a useful indication of the efficiency of the amalgamator train when comparing runs. Under the column headed "Filter", the topmost figure for each run gives the number of micrograms of mercury found in the filter for that run. Under this figure the total weight increase of the filter (weight of particulates collected on the filter) is given in grams.

2- Sampling Train Configuration

The initial runs (1 - 16) of the field study were performed to determine the optimum combination of amalgamators, empty impingers, and "scrubber" (a liquid-filled impinger ahead of the amalgamator train to help remove

moisture, sulfuric acid mist, etc.). The train configuration was varied for each run and each combination was generally done in duplicate and in random order. Sampling rate was 0.5 CFM.

Runs 7, 11, 12, and 13 were performed without any scrubber solution ahead of the amalgamator train. The configuration used and the relative distribution of the mercury found in the amalgamators is given below in Table 2.

TABLE 2

Sampling Train Configuration

Run	Configuration	Hg Distribution on Amalgamators (%)		
13	AAAEEK	28.1	32.2	39.8
12	EAAAEK	81.5	10.9	7.6
7	EEAAAK	45.5	48.2	6.2
11	"	86.9	7.5	5.6

The results suggested that maximum mercury pickup by the first amalgamator would be obtained in position "B" or "C".

3- Initial Scrubber Solution

Runs 1, 2, 4, 5, and 6 were performed using 250 ml of distilled water for a scrubber in position "A", with the amalgamator train starting at position "B". Runs 8 and 14 were performed in the same manner but with

an empty impinger in position "B" and the amalgamator train starting at Position "C". The results from these runs are given in Table 3.

TABLE 3

Distilled Water as the Scrubber

Run	Configuration	Hg Distribution on Amalgamators (%)		
1*	HAAAK	57.4	16.9	25.6
2*	"	96.7	2.4	1.0
4*	"	24.4	61.7	13.0
5*	"	47.0	33.0	20.0
6	"	72.6	8.1	19.2
8	HEAAAK	68.1	31.3	0.5
14	"	34.1	14.6	51.2

*The pump ran very erratically during these runs.

These results suggested that, within the limits of the reproducibility obtained there was no obvious advantage for either of these configurations over the other in terms of train efficiency; both produced at least one very good run (e.g., Runs 2,8) and some poor runs (5, 14). The cause of the inconsistent results obtained with these and other of the earlier runs was later discovered to be contamination of the gold chips caused by some substance evolved from the quartz wool plugs during the pre-firing of the amalgamators. This problem and its solution is discussed in more detail in Section 5, Critical Parameters.

It was noted that a significant amount of condensate was collected in the "B" position, while the "C" position showed very little condensate. This was observed whether Position A contained a scrubber or an empty impinger. It was therefore decided to adopt the practice of starting

the amalgamator train at the "C" position to minimize condensation in the amalgamators. The scrubber solution in the "A" position was found to collect a significant amount of mercury. Some mercury was also found in the condensate collected in the empty "B" impinger. It was decided to try a 1% solution of $SnCl_2$ as the scrubber solution to see if this would minimize the retention of mercury in the scrubber. Two methods were tried to accomplish this. In the first method, the impinger in the "A" position was simply filled with 250 ml of 1% $SnCl_2$ in 2-½% HCl. In the second method, 250 ml of distilled water were used in the "A" impinger and at the end of the run about 13 ml of a 20% $SnCl_2$ in 50% HCl solution were added to the inlet of the "A" impinger and about 3-5 CF of air was drawn through the train at that point to aerate the reduced mercury onto the first amalgamator. The results of these runs are given in Table 4.

TABLE 4

Stannous Chloride as the Scrubber

Run	Configuration	Hg Distribution on Amalgamators (%)		
3	SAAAK	85.0	10.2	4.8
9	SEAAAK	67.6	14.7	17.6
15	"	23.6	43.5	33.1
10	(HS)AAAK	4.8	9.6	85.6
16	"	21.6	12.8	65.5

When the $SnCl_2$ solutions from the "A" position were taken for analysis, they were found to require a large addition of $KMnO_4$ for oxidation of the contents, increasing the blank correction required. After addition

of the required amount of permanganate, some precipitate was noted in the solution and the analysis of these solutions showed poorer reproducibility than analyses obtained from the distilled water scrubbers. The aeration attempt did not prove to be successful; the "A" solutions of Runs 10 and 16 were found to contain mercury even after the aeration step.

On the basis of these results it was decided that the use of $SnCl_2$ as the scrubber offers no advantage and may present a disadvantage over the use of distilled water. The results obtained on addition of the $SnCl_2$ followed by aeration suggested the possibility of mercury being washed through the train by $SnCl_2$ vapors or droplets carried from the first impinger. It was therefore decided to use only distilled water as the scrubber for the remainder of this work.

4- The Use of $KMnO_4$ Solutions

For most of the runs in this study a solution of $KMnO_4$ in 2% HNO_3 was used in one or two impingers as a back-up system to catch any mercury going through the amalgamator train. At the high levels of SO_2 encountered, a saturated solution of $KMnO_4$ was completely decolorized in 4 - 6 minutes, depending on the sampling rate, SO_2 concentration, etc. It was found to be most practical to prepare the backup impingers using $KMnO_4$ as follows. The HNO_3 and distilled water was added to the impinger "shell" (250 ml for sampling rates of 0.5 CFM or less; 150 ml for sampling rates above 0.5 CFM) and then sufficient solid $KMnO_4$ was

weighed out and added to the water (about 3-5 grams per CF of sample to be taken). The resulting solution contained excess $KMnO_4$ crystals, but these dissolved as the solution was reduced during sampling.

Several problems were encountered with the use of $KMnO_4$ for back-up solutions.

1. It was apparent that more than two of the permanganate backups would be required to catch all of the mercury in those cases where a substantial quantity of mercury was passing through the amalgamator train. For example, Runs 47-62 were made using two $KMnO_4$ back-up solutions in series. In these runs some mercury was usually found in the second permanganate solution, although normally less than the amount found in the first one.

   Eight impingers and amalgamator units were already being used in the train and the pressure drop in the train was great enough so that the pump was only drawing about 0.7 CFM at maximum effort (pump vacuum at 25 inch Hg).

2. Since the permanganate backups were just before the silica gel, carryover from these solutions into the silica gel often completely ruined it in about 5-10 minutes. At flow rates above 0.5 CFM the volume in the permanganate impingers had to be reduced to 150 ml in order to avoid serious loss from violent "bumping". The heat of reaction as the $KMnO_4$ was reduced by the SO_2 (the permanganate impingers became quite warm to the touch) aggravated the carryover problem and caused impinger temperatures to go as high as 115°F after 15 minutes of sampling.

3. When longer sampling times of 10-15 minutes and/or higher sampling rates called for large amounts of $KMnO_4$ (50-80 grams) in 150 ml of water, the solution resembled a thick paste after the run. The efficiency of such a "solution" is very questionable.

In spite of these problems encountered with the permanganate solutions, it was felt that they could be made to yield some useful information for our purposes. The use of more than two permanganate backups

was not felt to be practical at this point. Instead, it was decided to use the data obtained from one or two permanganate backups as a check on the performance of the amalgamator train, with an understanding of its limitation as pointed out above. In other words, it was decided that the highest priority should be to improve the performance of the amalgamator train. If the amalgamation train could be made efficient enough, one or two permanganate backups would prove the point; if the amalgamators could not be made efficient enough, neither system would be practical. Subsequent results vindicated this approach to the problem.

5- Critical Parameters

Using the optimum train configuration, HEAAAK (determined as described above), a series of five-minute runs was performed at various sampling rates in the range of 0.211 to 0.833 CFM to see if the sampling rate had any effect on the collection efficiency of the amalgamators (Runs 17-30). The results were inconsistent. Some runs where the amalgamator sequence showed an orderly progression in the percentage distribution of mercury also showed a significant percentage of the mercury passing through the amalgamator train, as shown by the amount of mercury found in the permanganate backup solution (e.g., Runs 17 and 24).[13]

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[13] A useful way to compare this aspect of total train efficiency between runs is the figure given in the Data Table, Part B, under the column headed "Total Hg". Under the figure for the total mercury found in the train is a figure which represents the percentage of that total found ahead of the permanganate solutions.

Some runs showed a recovery ahead of the permanganate of 95% or more, but the distribution of mercury among the amalgamators appeared to be nearly randomn (e.g., Runs 25, 27). Neither the distribution of mercury in the amalgamators nor the percentage of mercury found ahead of the permanganate backups showed a clear relationship to sampling rate.

Runs 31-36 were performed using the same train configuration as above, the sampling times being varied from one to twenty minutes at a sampling rate of approximately 0.5 CFM. The results of this series showed the same kind of inconsistency in results as above. For example, the percentage of mercury found ahead of the permanganate averaged less than that found in Runs 17-30, although both shorter and longer sampling times were used. In this series of runs, only about 60% of the mercury was recovered ahead of the permanganate solutions. In an attempt to improve on this figure several variations in the system were tried.

Runs 37-40 were made using 33 grams of gold in each amalgamator (an increase of 65% in the total amount of gold in the train for Runs 37 and 38). In Runs 39 and 40, the amalgamator train was moved back one position; in Run 40 and extra scrubber was inserted to give the sequence:

Run 39	HEEAAK	(66 gm gold total)
Run 40	HHEAAK	(66 gm gold total)

None of these variations produced any improvement in the performance of the amalgamator train.

Runs 41-51 were performed using five amalgamators in series, starting from the filter, each containing 20 grams of gold. It was hoped that distribution data from the increased amount of total gold divided among the five amalgamators might provide an insight into the cause of the inconsistent results obtained up to this point. Sampling times of five to thirty minutes and sampling rates of about 0.3 to 0.7 CFM were employed. Inspection of mercury distribution data for these runs showed that the expected orderly progression of mercury concentration through the amalgamator train was largely absent. The percentage of mercury recovered ahead of the permanganate ranged from 33% to 93%. Since previous work had given better results than this, using less gold, it was tentatively assumed that the gold was being effectively "poisoned", either by some substance from the stack, or by some step in the handling procedure. The lack of correlation between sampling time or rate, and the efficiency of the train discounted the former possibility, so we turned our attention to the handling procedure being used. To see if the trouble was coming from the pre-firing step, Run 49 was performed using amalgamators prepared in the same manner as before, except that the pre-firing step was eliminated. The gold was placed in the amalgamators directly from the firing crucibles after cooling. This simple modification proved to be the key to the problem: the first amalgamator of Run 49 picked up 92% of the mercury found in the amalgamator train. This was a much higher figure than any obtained in a previous run. Runs 50 and 51 were performed in the manner previously used for the second and third runs of any day; the

amalgamators were placed in the train after the normal firing procedure used for the previous run (first run of the day). The results showed that firing the amalgamator with the quartz wool plug in place causes a progressive decrease in that amalgamator's ability to remove mercury from the sample stream. To make sure of this point, Runs 52 and 53 were performed using gold fired overnight in the oven and not pre-fired. Run 54 was performed using the same gold, amalgamators, and quartz wool plug as Run 53. The pertinent data from Runs 49-54 is shown in Table 5.

TABLE 5

The Effect of Firing the Amalgamators in the Presence of the Quartz Wool Plug

Run	Fired with Quartz Wool Plug in Place	Percentage of Total Amalgamator Mercury Found on First Amalgamator	Percentage of Total Mercury Found Ahead of Permanganate
49	No	92.2	
50	Yes	64.0	52.6
51	Yes	47.9	64.2
52	No	94.4	93.6
53	No	94.8	95.8
54	Yes	41.6	45.7

From these results and the results of subsequent work, the following conclusions were drawn:

1. The heating of the quartz wool plug during firing of the gold causes the plug to give off some substance which collects on the surface of the gold (presumably while the gold is cooling) partially coating it and thus decreasing the effective surface area available for amalgamation of mercury from a flowing gas stream.

2. In the laboratory, a piece of the quartz wool was weighed, fired for two days in a crucible in the refractory oven and then reweighed. The results were:

weight before firing	0.2422 g
weight after firing	0.2408 g
weight loss	0.0014 g

percentage weight loss = 0.58%

Only a small amount of this volatile material is necessary to desensitize the gold.

3. The condition of the gold (cleanness of the surface) is probably the single most important factor affecting the efficiency of the amalgamators.

Firing in an oven seems to be the best way to clean the gold before use and between uses.

4. Since the condition of the gold was found to be such a large factor in the performance of the amalgamation train, it was obvious that the previous study of the dependence (if any) of collection efficiency on sampling rate and sampling time should be at least partially repeated using only freshly (oven) fired clean gold.

6- Collection Efficiency of the Amalgamators

The collection efficiency of the amalgamator train was studied as a function of sampling rate, sampling time, and the total amount of mercury collected. This was done for a train of three amalgamators containing 20 grams of gold each, and for trains of four and five amalgamators, each containing 30 grams of gold. Clean gold, not fired in the presence of the quartz wool plug, was used for these studies. The collection efficiencies of Runs 55-72 are presented in Table 6.

a. Theory

Consider a series of identical amalgamators (the same size and shape, each containing the same amount of gold, the same distribution of particle size, void fraction, etc.). If we assume that the amount of gold is much larger than the amount of mercury to be collected (i.e., the accumulation of mercury on an amalgamator during sampling does not alter its collection properties; that it is operating well below capacity), a relationship can be derived between the ratio of mercury found in any two adjacent amalgamators and the collection efficiency of one or any total number of amalgamators.

Let r = the fraction of mercury entering an amalgamator which is trapped by the gold. This can be called the "trapped fraction" of a single amalgamator.

then $(1 - r)$ = the fraction of mercury passing through that amalgamator which is not trapped by the gold. This can be called the "escape fraction" of a single amalgamator.

If n amalgamators are connected in series, the fraction of the total mercury passing through the n^{th} amalgamator, $f_{e,n}$, is given by:

TABLE 6

Collection Efficiencies

Run No.	Metered Gas Volume	Percent of Amalgamated Mercury in each Position					Percent of Mercury Recovered before Permanganate Backup
		C	D	E	F	G	
55	1.533	88.6	5.7	5.7	K	K	96.9
56	3.609	92.3	5.7	2.0	K	K	96.6
57	3.146	90.7	7.7	1.6	K	K	99.0
58	4.899	93.3	5.4	1.2	K	K	97.6
59	7.240	91.3	5.9	2.8	K	K	94.5
60	6.861	67.6	25	7.4	K	K	95.1
61	10.738	59.3	31.8	8.9	K	K	91.1
62	6.404	74.4	21.4	4.2	K	K	89.1
63	3.156	76.1	1.1	0.7	0.4	21.6	99.7
64	4.897	86.7	3.2	3.5	3.4	3.2	*
65	2.311	82.1	0.0	0.0	3.1	14.8	98.8
66	7.830	98.7	0.2	0.1	0.0	1.0	*
67	8.838	97.1	1.0	0.6	0.6	0.7	*
68	10.406	89.0	10.3	0.4	0.3	SG	*
69	3.816	84.8	13.8	0.6	0.9	K	100.0
70	4.742	79.1	16.5	2.4	1.9	K	98.3
71	4.215	61.5	9.5	10.5	10.7	7.8	*
72	6.923	79.4	12.3	2.8	3.0	2.5	*

K - Acidic Permanganate Scrubber
SG - Silica Gel
* - Train did not contain an acidic permanganate scrubber

$$f_{e,n} = (1 - r)^n \qquad (1)$$

The fraction of the total mercury trapped by the n^{th} amalgamator, $f_{t,n}$, is equal to the fraction passing through the $(n-1)^{th}$ amalgamator times r:

$$f_{t,n} = r(1 - r)^{n-1} \qquad (2)$$

The expansion of terms (1) and (2) for each amalgamator is given in Table 7.

TABLE 7

Theoretical Distribution of Mercury in a Series of Amalgamators

Amalgamator No.	Fraction of Total Trapped by Amal. $f_{t,n}$	Fraction of Total Through Amal. $f_{e,n}$
1	r	$1-r$
2	$r-r^2$	$1-2r+r^2$
3	$r-2r^2+r^3$	$1-3r+3r^2-r^3$
4	$r-3r^2+3r^3-r^4$	$1-4r+6r^2-4r^3+r^4$
5	$r-4r^2+6r^3-4r^4+r^5$	$1-5r+10r^2-10r^3+5r^4-r^5$
.	.	.
.	.	.
n	$r(1-r)^{n-1}$	$(1-r)^n$

Similarly to Equation (2), the fraction of the total mercury trapped by the $(n-1)^{th}$ amalgamator, $f_{t,n-1}$, is equal to the fraction passing through the (n -2)nd amalgamator times r:

$$f_{t,n-1} = r(1 - r)^{n-2} \qquad (3)$$

If T = the total μg of mercury passing through the train, the μg of

mercury trapped by the n^{th} amalgamator, t_n, is given by

$$t_n = Tf_{t,n} \tag{4}$$

$$t_n = T\, r(1-r)^{n-1} \tag{5}$$

and the μg of mercury trapped by the (n -1)th amalgamator is given by

$$t_n = T\, f_{t,n-1} \tag{6}$$

$$t_{n-1} = T\, r(1-r)^{n-2} \tag{7}$$

Dividing (5) by (7) we obtain:

$$\frac{t_n}{t_{n-1}} = \frac{T\, r(1-r)^{n-1}}{T\, r(1-r)^{n-2}} = (1-r) \tag{8}$$

Thus, the "escape fraction", (1 -r), can theoretically be obtained directly from the ratio of total mercury found in any two adjacent amalgamators. In actual practice, however, where the "escape fraction" is low, only the first and second amalgamators in the series show enough mercury to give a value of t_1 and t_2 with sufficient relative accuracy to calculate a meaningful value for (1 -r). For this reason, calculations of t_n/t_{n-1} in this report have been confined to the first two amalgamators.

The fraction of the total mercury trapped by the whole series of n amalgamators, $F_{t,n}$, is given by the sum

$$F_{t,n} = f_{t,1} + f_{t,2} + f_{t,3} + \cdots\cdots f_{t,n} \tag{9}$$

Since $$F_{t,n} + f_{e,n} = 1 \quad (10)$$

Substituting (1) into (10) we obtain:

$$F_{t,n} = 1 - (1 - r)^n \quad (11)$$

Equation (11) can be used to calculate:

A. The maximum "escape fraction" permissible to achieve a given percentage of total mercury recovery for any number of amalgamators.

B. The percentage of total mercury recovery for an experimentally obtained "escape fraction" when using any given number of amalgamators.

C. The number of amalgamators necessary to obtain a given percentage total recovery if the "escape fraction" for the amalgamators is known.

For example, if we wish to obtain a 95% total recovery using three amalgamators, from equation (11),

$$F_{t,n} = 1 - (1 - r)^3 = 0.95$$

$$(1 - r)^3 = 0.05$$

$$(1 - r) = \sqrt[3]{0.05}$$

$$t_2/t_1 = (1 - r) = 0.368$$

We must obtain a value for t_2/t_1 of less than 0.368 in order to achieve 95% recovery using three amalgamators in the train.

The maximum t_2/t_1 permissible to achieve a 95% total mercury recovery for any number of amalgamators is given in Table 8.

TABLE 8

Maximum Escape Fraction for 95% Recovery

No. of Amalgamators	Maximum t_2/t_1 for 95% Recovery
2	0.224
3	0.368
4	0.473
5	0.549

b. 20 grams of Gold per Amalgamator

For Runs 55-62, the train sequence was HEAAAKK with 20 grams of gold in each amalgamator. Sampling times of 5, 10, and 15 minutes, and sampling rates from 0.307 to 0.722 CFM were used. Since Runs 49, 52, and 53 were also performed with 20 grams of gold not fired in the amalgamator before use, the data from these runs is also included here. All of these runs were found to give much better and more consistently good results than those obtained previously. The amount of mercury found showed a progressive and orderly decrease through the series of amalgamators (see Table 6); the first one retaining about 90% of the total "amalgamator mercury" and the last one about 1-6%. The percentage of mercury recovered ahead of the permanganate backup solution showed a corresponding improvement (the median value was 95%).

In order to discover whether the collection efficiency of the amalgamators showed any dependence on the sampling rate, the ratio of t_2/t_1 was calculated for each of these runs and plotted against the sampling

rate, as shown in Figure 16. The resulting curve showed almost no dependence of the collection efficiency on sampling rate within the range of sampling rates studied.

The ratio t_2/t_1 was also plotted against $t_2 + t_1$ as shown in Figure 17, to see if there was any decrease in collection efficiency as the amount of mercury collected increased (saturation effect). This plot showed no dependence of collection efficiency on the micrograms of mercury collected. The dotted lines shown on Figures 16 and 17 represent a t_2/t_1 value of 0.368, corresponding to a total amalgamator train efficiency of 95% for 3 amalgamators.

Figures 16 and 17 both show all values of t_2/t_1 clustered below $t_2/t_1 = 0.1$, except for Runs 60-62, which are noticeably higher. The discrepancy of these runs may perhaps be explained by reference to some observations made while these samples were being taken and then fired. During the cleanup of Run 60, a considerable quantity of what appeared to be a black, tarry substance was found in the cyclone and filter assembly. This substance was not soluble in water but was soluble in acetone. In firing each of the amalgamators from this run, a quantity of smoke was evolved which condensed on the portion of the amalgamator tube above the gold as an oily film. On Run 61, a considerable quantity of the black tarry substance was found condensed in the first amalgamator tube after it had been fired and the quartz wool plug was quite dark looking. The filters from Runs 60-62 were also much darker in appearance than usual. These observations suggest that

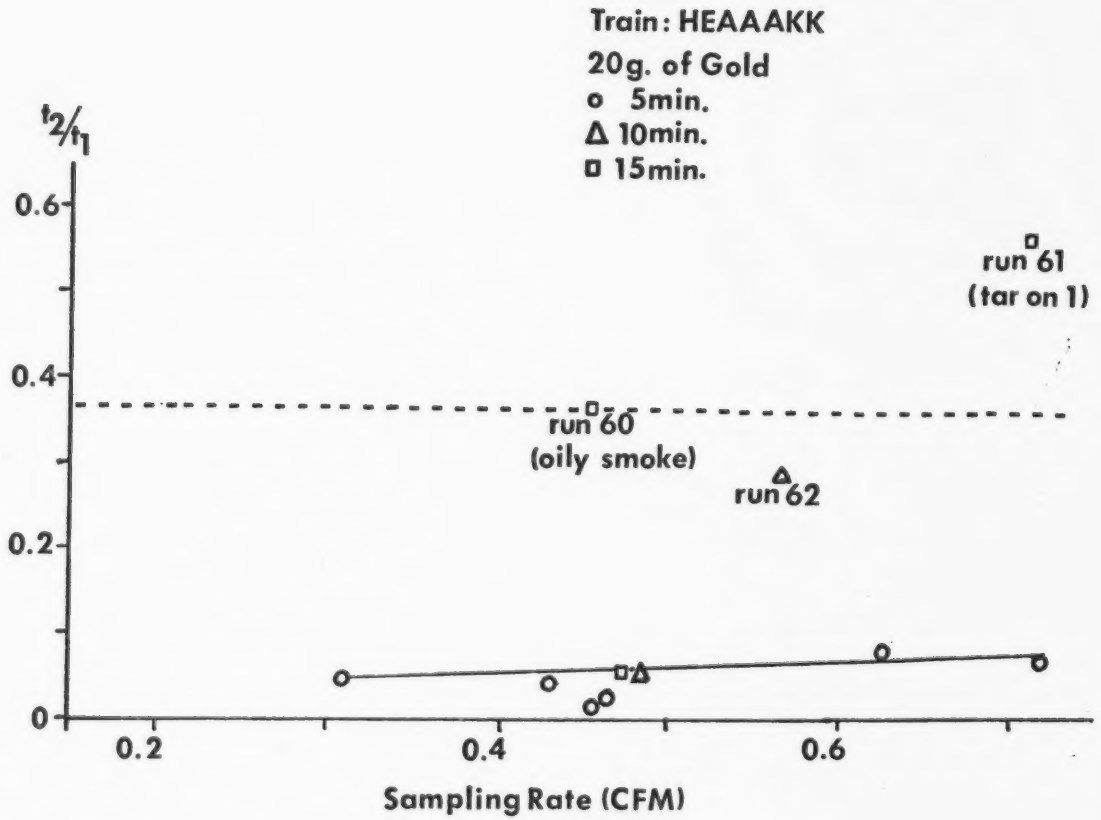

Figure 16. Collection Efficiency vs. Sampling Rate for 20 Grams of Gold per Amalgamator.

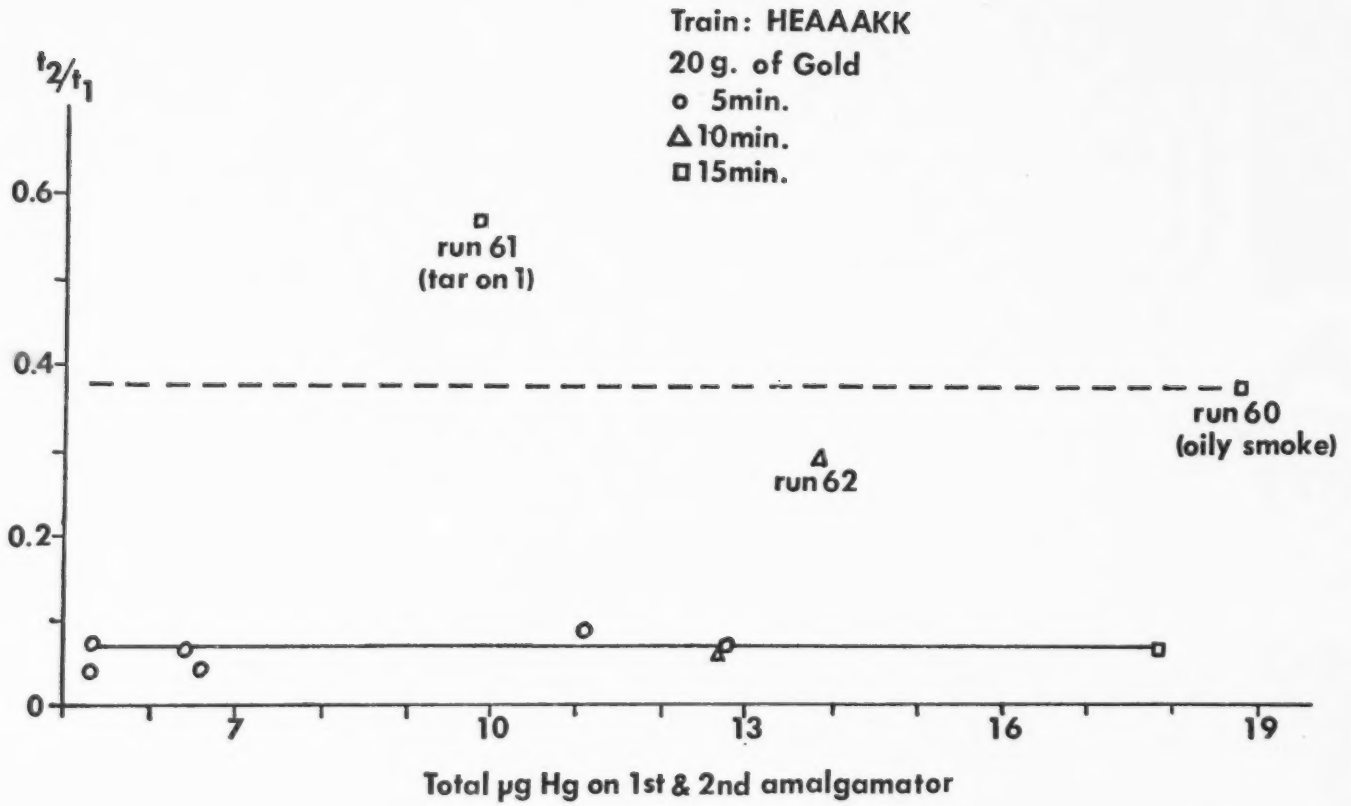

Figure 17. Collection Efficiency vs. Total Mercury Collected for 20 Grams of Gold per Amalgamator.

some abnormal variation in the ore being roasted, or a malfunction in some part of the equipment at the plant may have been responsible for releasing some high boiling organic substance into the gas stream where it was collected by the sampling unit and a portion of it was deposited on the gold. This seems the most likely explanation, as the first amalgamator in each series seems to be the one most affected, the t_3/t_2 ratio in each case being less than t_2/t_1 for the same run. In this connection it is interesting to note that the percentage of mercury recovered ahead of the permanganate backups did not decrease very much for these three runs, the figures for Runs 60, 61, and 62 being 95.1%, 91.1%, and 89.1%, respectively.

These results point out once again the fundamental importance of the condition of the gold, and suggest that it would be wise to employ enough gold in the amalgamator train to provide a generous reserve capacity, as the deposition of any oil or tar on the gold (which may be inadvertent or unavoidable in an actual sampling situation) will greatly decrease its collection efficiency. Concluding that this approach would prove to be the best one to the problem of obtaining consistently high collection efficiency while sampling under actual field conditions, we made a series (63-72) using what was considered to be our "optimum train."

c. 30 grams of Gold per Amalgamator

Thirty grams of the gold chips used in this study make a column 3.2 - 3.7 cm high in the amalgamator tube. This was about the tallest

column of chips which could be uniformly heated by the present coil in the induction furnace (other sized coils can be used in this furnace if desired). Since a total of only 160 grams of gold was available for this study, we made a series of runs (63 - 72) using a train of either four or five amalgamators with thirty grams of gold in each one. Of this series, Runs 63, 65, 69, and 70 also contained a permanganate backup solution to check the efficiency of the amalgamator train. Sampling times of 5, 10, and 15 minutes were used and the sampling rate was varied from 0.281 to 0.763 CFM. Run 72 was a 15 minute run taken under isokinetic conditions. These runs showed a large percentage of the total "amalgamator mercury" on the first amalgamator and an orderly decrease in mercury through the train. The total percentage of mercury collected ahead of the permanganate backups was very high, ranging from 98 to 100%. The ratio t_2/t_1 vs. sampling rate is shown in Figure 18. From this experimental data, there does not seem to be any dependence of collection efficiency on the flow rate. The ratio t_2/t_1 is also plotted against $t_2 + t_1$ in Figure 19. Again, there does not appear to be any dependence of collection efficiency on the total amount of mercury collected, at least within the range studied. The collection efficiency also appears to be independent of the sampling time used, and our experience with these and earlier runs (e.g., Runs 36, 38, 46) does not suggest that 15 minutes is the maximum feasible sampling time.

The data from Runs 63-72 shown in Figures 18 and 19 show the same kind of clustering referred to above. The values of t_2/t_1 for

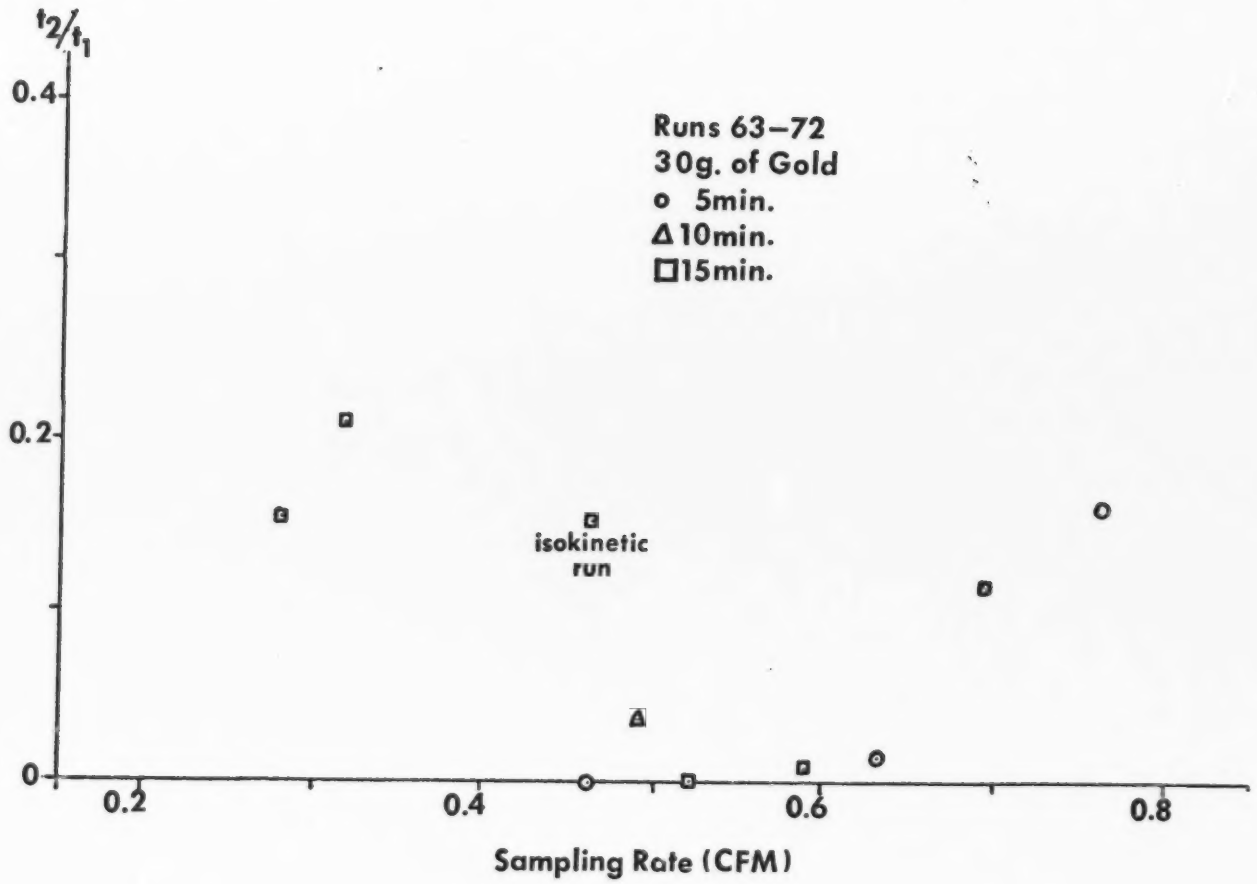

Figure 18. Collection Efficiency vs. Sampling Rate for 30 Grams of Gold per Amalgamator.

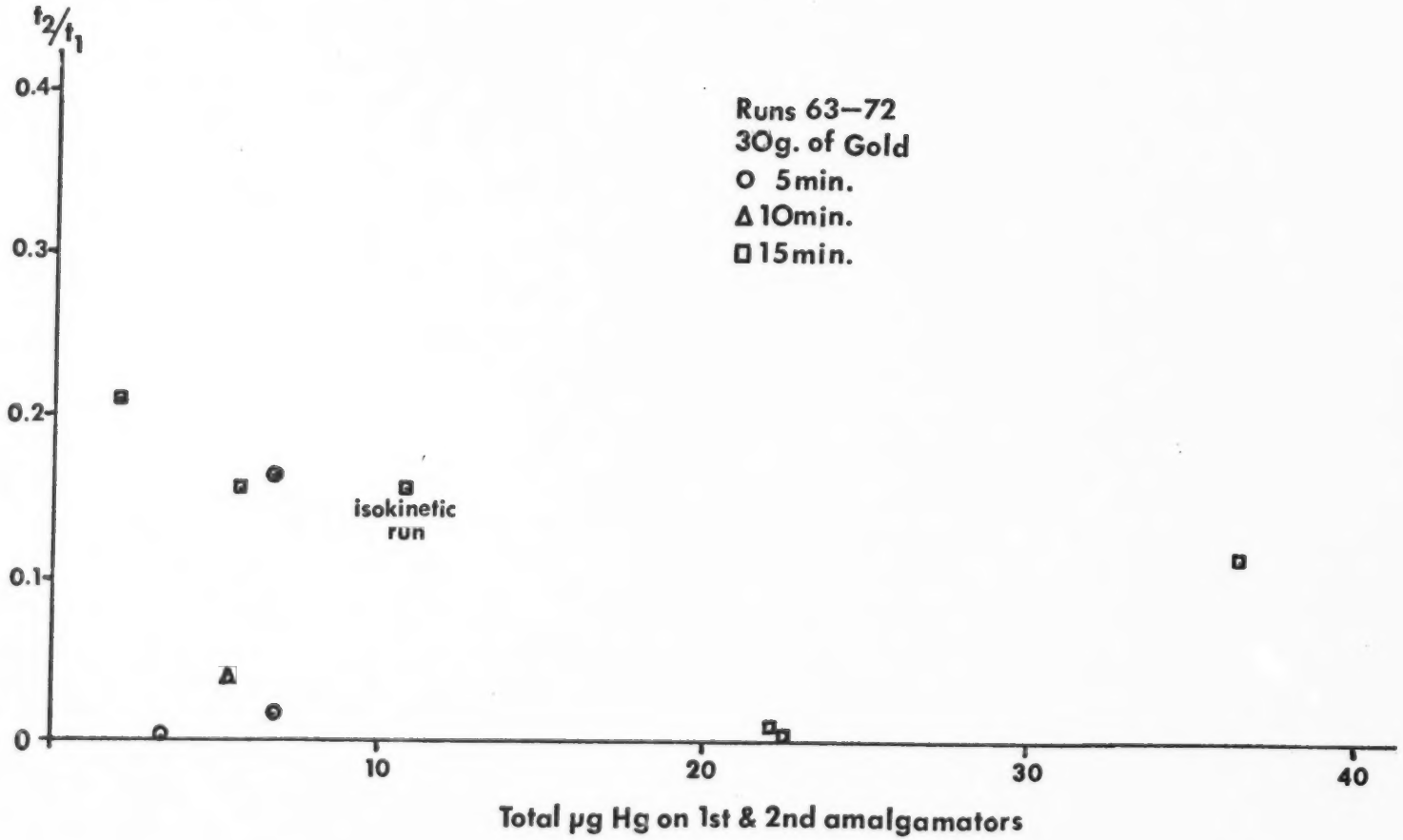

Figure 19. Collection Efficiency vs. Total Mercury Collected for 30 Grams of Gold per Amalgamator.

Runs 63-67 are clustered below 0.05, while t_2/t_1 for Runs 68-72 are all in the range of 0.11 to 0.21. All values were, however, well under the t_2/t_1 ratio of 0.47 corresponding to 95% efficiency for the train (see Table 8).

Run 68 was taken at about 1:30 pm on December 6, 1972. The ASARCO plant had been having some trouble with their acid recovery plant, which had started up around noon after having been shut down in the morning. The roaster operator on duty informed us at that time that one of the two electrostatic precipitators had not been working for some time and that the other one was not working properly. This could explain the slightly lower collection efficiency obtained on this and the following runs.

7- Sources of Error

The errors which could be encountered in the application of this method to an actual sampling situation might be broadly classified as sampling errors or analytical errors.

a. Sampling Errors

The most likely sampling error, in our opinion, is the failure to collect all of the mercury in the sample stream due to insufficiently clean gold. Contamination of the gold from the gas stream being sampled is, of course, minimized by the use of the normal cyclone and filter assembly. The wet scrubber solution next to the filter followed by an empty impinger is also an aid here. In our experience these items

undoubtedly help but do not eliminate the problem of gold contamination during sampling. Our most successful approach has been to use enough gold in enough amalgamators to provide a reserve capacity in case such contamination does occur. Examination of the data from the amalgamator train should enable one to tell if such contamination has indeed occurred, and allow at least a rough estimate of its severity to be made. By using five amalgamators in the series, each containing 30 grams of gold, we were able to obtain very high train efficiencies, in spite of a certain amount of gold contamination (at least for 15 minutes of sampling time). We do not know how our sample source compares to others with respect to such contamination problems.

b. Analytical Errors

Special precautions should be taken to avoid mercury contamination of the glassware used. The normal precautions of good analytical techniques apply here. Reagent blanks and permanganate blanks should be periodically checked and appropriate records kept. We used one lot of $KMnO_4$ for our work. Careful determination of the mercury blank for the lot used in this study gave a value of 0.012 μg of mercury per gram of $KMnO_4$ and this value was used as a correction factor for the permanganate backup solution analyses. In addition, daily blanks were taken from the working solution of 3% $KMnO_4$, 10% HNO_3 used for preserving the samples, and these blank corrections applied to the analytical results obtained.

For earlier runs of this study, a single piece of tygon tubing, about 18 inches long, was used to connect the amalgamator to the bubbler

while firing the amalgamators. This piece of tubing was washed out along with the bubbler between runs. On Runs 63 and 65 some contamination of the last amalgamator was suspected due to the unexpected and otherwise unexplainable amount of mercury found in the last position. It was suspected that the tygon tubing was adsorbing mercury when high concentrations were present in the nitrogen stream (from firing the first amalgamator of the previous run) and desorbing it again during subsequent firings when heated nitrogen (containing little or no mercury) was flowing through it. The washing procedure was not cleaning it thoroughly. On Runs 67-72, the tygon was shortened to 2-½ inches (to minimize loss by adsorption on the tygon) and replaced with a new piece for each run (to eliminate contamination of the solution obtained by firing the last amalgamator in the train, which was also the first one fired in the series). There was no further evidence of cross contamination between subsequent runs.

8- Application to Isokinetic Sampling

Isokinetic sampling is usually performed at a sampling rate of 0.5 to 0.8 CFM. Since quantitative recovery of mercury from the gas sample was obtained at these rates, and in view of the independence of recovery on sampling rate, there is no reason why this procedure could not be used for isokinetic sampling. Run 72 was, in fact, taken isokinetically, and the data sheets for this run are included in Appendix III.

CONCLUSIONS

The results of this study show that the gold amalgamation technique, for the collection of mercury from a gas stream containing a high percentage of SO_2, can achieve quantitative collection efficiencies at the sampling rates normally used for isokinetic sampling. Figures 16 and 18 show quantitative collection independent of flow rate in the range of 0.3 to 0.8 CFM. Isokinetic sampling is carried out in the range of 0.5 to 0.8 CFM showing that the procedure developed in this study can be used isokinetically. One run was made under actual isokinetic conditions, and the collection efficiency achieved was the same as the efficiencies obtained with the same equipment and procedure under non-isokinetic conditions. Since some mercury was always found in the probe, cyclone and filter assembly, a sample taken for the purpose of establishing total emission of mercury from a source should be taken isokinetically to insure representative sampling. The standard isokinetic sampling procedure is to sample for about five minutes at each traverse point so that total sampling time is about one hour. Although sampling times of 15 minutes or less were used with the train and procedure as finally optimized in this study, none of the results obtained suggest that longer sampling times could not have been used with equally good results.

Some of the data obtained suggests that collection efficiencies are lowered by volatile materials which get through the cyclone and filter and one initial wet scrubber and coat the gold. In this study a series of five amalgamators, each containing 30 grams of gold chips, provided a

sufficient reserve capacity to compensate for this problem as it was encountered in this stack. Since other stacks on other plants could be significantly different with respect to the amount of such volatiles, it might be advisable (as least initially) to have some kind of feedback on the sampling efficiency obtained so that additional samples could be taken if necessary before equipment and personnel have vacated the sampling site. This could be accomplished by on-site analysis of a portion of the samples obtained.

Some suggestions are also offered here for certain improvements in the equipment which the authors feel may make the sampling and analysis operations easier and more efficient. For best results from the laboratory analyses, an all glass system for the mercury analysis is recommended. The use of tygon tubing in the system should be minimized or avoided: tygon has been found by the authors to absorb (and desorb) mercury from an air stream. Other workers have also found that both tygon and teflon absorb mercury.[14]

A simpler (less expensive and easier to clean) bubbler could be designed for use in firing the amalgamators. The presently used bubbler assembly should be reserved for the laboratory analysis procedure, which it was originally for.

The levels of SO_2 encountered and the procedure of drawing it through the pump is hard on the sampling equipment, especially the pump. It may be

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[14] ASTM Subcommittee D-5.21, Trace Element Task Group, Methodology Subgroup, meeting of May 25, 1972, private communication.

necessary to dismantle and clean it after each run to insure dependable operation. It may also be necessary to make some parts of the equipment from corrosion-proof materials.

A larger sampling box which could hold 8 - 10 impingers in the ice bath without excessive crowding would be useful and would have the advantage that an extra scrubber or empty impinger could be inserted ahead of the gold train if such a change was found necessary to insure cleanness of the gold during sampling on an especially dirty stack.

APPENDIX I

TABLE 9

Part A. Field Parameters:

RUN # DATE TIME	SAMPLING TIME	BAROMETRIC PRESSURE	AMBIENT TEMP.	STACK TEMP. (T_s)	%SO_2	STATIC PRESS. (P_s)	VELOCITY HEAD (ΔP_s)	ORFICE PRESS. (ΔH)	IMPINGER TEMP.	DRY GAS TEMP. (T_m)	METERED GAS VOL. (V_m)	SAMPLING RATE
1972	minutes	in. Hg	°F	°F		in. H_2O	in. H_2O	in. H_2O	°F	°F	Cu. ft.	CFM
1 10/17 4:16 pm	5.0		60	440		+ 0.05			60	58.5	2.152	.430
2 10/19 11:38 am	7.0		41	460		+ 0.32			50	44.0	2.856	.407
3 10/19 4:04 pm	7.0		41	480		+ 0.32			55	45.5	3.014	.430
4 10/20 10:53 am	10.0	29.48	41	460		+ 0.04			<50	48.0	4.136	.414
5 10/20 2:35 pm	12.0	29.48	50	460		- 0.13			67.5	57.5	6.379	.532
6 10/20 4:05 pm	15.0	29.48	48.2	460		-0.06			56.0	58.0	6.022	.401
7 10/23 2:18 pm	5.0	28.84	73.4	430		-0.41			60.0	67.5	2.585	.517

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RUN # DATE TIME	SAMPLING TIME	BAROMETRIC PRESSURE	AMBIENT TEMP.	STACK TEMP. (T_s)	%SO_2	STATIC PRESS. (P_s)	VELOCITY HEAD (ΔP_s)	ORFICE PRESS. (ΔH)	IMPINGER TEMP.	DRY GAS TEMP. (T_m)	METERED GAS VOL. (V_m)	SAMPLING RATE
1972	minutes	in. Hg	°F	°F		in. H_2O	in. H_2O	in. H_2O	°F	°F	Cu. ft.	CFM
8 10/23 4:03 pm	5.0	28.84	62.6	430		- 0.26			60	68.0	2.391	.478
9 10/24 10:44 am	5.0	29.12	50.0	460		- 0.67			50	51.5	2.477	.495
10 10/24 12:03 pm	5.0	29.12	44.6	470		0			<50	50.5	2.355	.471
11 10/24 2:20 pm	5.0	29.12	45.5	480		+ 0.36			50	49.0	2.549	.510
12 10/24 3.47 pm	5.0	29.12	45.5	480		+ 0.20			50	50.0	2.532	.506
13 10/30 10:16 am	5.0	29.30	46.4	480	6.0	+ 0.12		0.92	50	52.0	2.529	.506
14 10/30 11:49 am	5.0	29.30	50.0	495	6.4	- 0.10		0.86	50	50.0	2.485	.497

RUN # DATE TIME	SAMPLING TIME	BAROMETRIC PRESSURE	AMBIENT TEMP.	STACK TEMP. (T_s)	$\%SO_2$	STATIC PRESS. (P_s)	VELOCITY HEAD (ΔP_s)	ORFICE PRESS. (ΔH)	IMPINGER TEMP.	DRY GAS TEMP. (T_m)	METERED GAS VOL. (V_m)	SAMPLING RATE
1972	minutes	in. Hg	°F	°F		in. H_2O	in. H_2O	in. H_2O	°F	°F	Cu. ft.	CFM
15 10/30 2:15 pm	5.0	29.30	52.7	490	6.4	- 0.17		0.95	50	53.5	2.409	.482
16 10/30 3:45 pm	5.0	29.30	50.0	495	6.6	0		0.93	50	54.0	2.561	.512
17 10/31 10:17 am	5.0	29.30	46.4	520		+ 0.77		0.21	50	46.0	1.292	.258
18 10/31 11:39 am	5.0	29.30	48.2	520		+ 0.91		0.30	50	49.0	1.867	.373
19 10/31 1:50 pm	5.0	29.30	50.0	370		+ 2.75		1.30	50	51.5	3.073	.615
20 10/31 3:35 pm	5.0	29.30	46.4	470		+ 1.50		1.75	50	49.5	3.526	.705
21 11/1 1:10 pm	5.0	29. 04	56.3	500	6.5	+ 0.14		2.20	50	60.5	4.033	.807

RUN # DATE TIME	SAMPLING TIME	BAROMETRIC PRESSURE	AMBIENT TEMP.	STACK TEMP. (T_s)	$\%SO_2$	STATIC PRESS. (P_s)	VELOCITY HEAD (ΔP_s)	ORFICE PRESS. (ΔH)	IMPINGER TEMP.	DRY GAS TEMP. (T_m)	METERED GAS VOL. (V_m)	SAMPLING RATE
1972	minutes	in. Hg	°F	°F		in. H_2O	in. H_2O	in. H_2O	°F	°F	Cu. ft.	CFM
22 11/1 2:42 pm	5.0	29.04	57.2	500	6.4	+ 0.28		0.24	50	62	1.465	.293
23 11/1 4:35 pm	5.0	29.04	57.2	500	6.8	0		0.80	50	62	2.495	.499
24 11/2 10:32 am	5.0	28.85	60.8	490	7.2	- 0.16		1.20	55	63.5	2.982	.596
25 11/2 12:04 pm	5.0	28.85	62.6	480	7.0	- 0.16		1.70	55	64	3.499	.700
26 11/2 3:35 pm	5.0	28.85	55.4	510	8.1	+ 1.01		0.17	55	60	1.054	.211
27 11/2 4:45 pm	5.0	28.85	59.9	510	8.3	+ 1.20		0.29	55	61	1.551	.310
28 11/3 11:53 am	5.0	29.06	60.8	500	8.0	- 0.36		0.89	60	65	2.620	.524

RUN # DATE TIME	SAMPLING TIME	BAROMETRIC PRESSURE	AMBIENT TEMP.	STACK TEMP. (T_s)	$\%SO_2$	STATIC PRESS. (P_s)	VELOCITY HEAD (ΔP_s)	ORFICE PRESS. (ΔH)	IMPINGER TEMP.	DRY GAS TEMP. (T_m)	METERED GAS VOL. (V_m)	SAMPLING RATE
1972	minutes	in. Hg	°F	°F		in. H_2O	in. H_2O	in. H_2O	°F	°F	Cu. ft.	CFM
29 11/3 2:05 pm	5.0	29.06	57.2	500	7.9	- 0.36		0.56	60	60.0	2.075	.415
30 11/3 3:22 pm	5.0	29.06	53.6	510	7.7	- 0.27		2.60	60	60.0	4.166	.833
31 11/8 11:10 am	1.0	29.06	44.6	500	7.4	- 0.56		0.90	<50	46.5	0.474	.474
32 11/8 1:36 pm	3.0	29.06	47.3	500	8.4	- 0.47		1.00	<50	48.0	1.632	.544
33 11/8 3:15 pm	5.0	29.06	46.4	500	8.4	- 0.41		0.71	50	49.0	2.306	.461
34 11/8 4:34 pm	10.0	29.06	47.3	510	8.0	- 0.34		0.83	50	50.5	5.232	.523
35 11/9 10:25 am	15.0	29.26	44.6	520	7.6	- 0.27 - 0.26 - 0.27		0.78 0.90 0.88	55 72.5 72.5	46.0 48.5 51.0	7.416	.494

RUN # DATE TIME	SAMPLING TIME	BAROMETRIC PRESSURE	AMBIENT TEMP.	STACK TEMP. (T_s)	$\%SO_2$	STATIC PRESS. (P_s)	VELOCITY HEAD (ΔP_s)	ORFICE PRESS. (ΔH)	IMPINGER TEMP.	DRY GAS TEMP. (T_m)	METERED GAS VOL. (V_m)	SAMPLING RATE
1972	minutes	in. Hg	°F	°F		in. H_2O	in. H_2O	in. H_2O	°F	°F	Cu. ft.	CFM
36 11/9 1:00 pm	20.0	29.26	45.5	525	7.6	- 0.14 - 0.16 - 0.24 - 0.28		0.82 0.97 0.88 0.86	50 75 87.5 85	48 52 54.5 56	10.021	.501
37 11/9 3:05 pm	15.0	29.26	46.4	520	7.6	- 0.33 - 0.34 - 0.36		0.79 0.89 0.86	65 75 85	50.5 54.5 57	7.428	.495
38 11/9 4:30 pm	20.0	29.26	44.6	520	7.7	- 0.42 - 0.41 - 0.41 - 0.43		0.91 0.96 0.93 0.91	50 67.5 80 75	50 53 56.5 59	10.293	.514
39 11/10 2:42 pm	20.0	28.90	53.6	510	7.5	- 0.54 - 0.52 - 0.53 - 0.55		0.58 0.81 0.90 0.92	65 105 100 85	55 65 72.5 77	9.647	.482
40 11/10 4:42 pm	20.0	28.90	59.0	520	7.5	- 0.50 - 0.52 - 0.54 - 0.55		0.89 0.88 0.87 0.85	<50 50 57.5 65	52 54.5 56.5 58.5	10.165	.508
41 11/13 11:33 am	15.0	29.04	50.0	510	6.6	- 0.12 - 0.06 0		0.85 0.92 0.91	<50 65 75	44 47 50.5	7.272	.485
42 11:13 2:36 pm	10.0	29.04	56.3	510	7.2	- 0.34 - 0.46		1.10 1.00	<50 55	45.5 47.5	6.137	.614

RUN # DATE TIME	SAMPLING TIME	BAROMETRIC PRESSURE	AMBIENT TEMP.	STACK TEMP. (T_s)	$\%SO_2$	STATIC PRESS. (P_s)	VELOCITY HEAD (ΔP_s)	ORFICE PRESS. (ΔH)	IMPINGER TEMP.	DRY GAS TEMP. (T_m)	METERED GAS VOL. (V_m)	SAMPLING RATE
1972	minutes	in. Hg	°F	°F		in. H_2O	in. H_2O	in. H_2O	°F	°F	Cu. ft.	CFM
43 11/13 4:40 pm	5.0	29.04	57.2	510	7.1	- 0.47		.95-1.5	<50	43.5	2.617	.523
44 11/14 10:36 am	15.0	28.70	44.6	520	7.7	- 0.38 - 0.37 - 0.36		0.36 0.28 0.29	<50 55 60	45.0 46.0 46.5	4.579	.306
45 11/14 1:16 pm	15.0	28.70	42.8	520	7.6	- 0.39 - 0.34 - 0.35		1.90 1.90 1.90	110 100 85	48.0 55.0 59.5	10.652	.710
46 11/14 3:25 pm	30.0	28.70	39.2	540	8.2	- 0.36 - 0.36 - 0.36 - 0.36 - 0.32 - 0.31		0.59 0.54 0.57 0.58 0.50 0.67	50 75 75 65 55 55	37.5 38.5 39 40 40.5 41.5	11.592	.386
47 11/15 12:22 pm	4.38	29.24	35.6	575	8.5	- 0.25		0.98	<50	36	2.140	.488
48 11/15 3:55 pm	5.0	29.24	35.6	560	8.6	- 0.25		.85-.90	<50	37.5	2.376	.475

RUN # DATE TIME	SAMPLING TIME	BAROMETRIC PRESSURE	AMBIENT TEMP.	STACK TEMP. (T_s)	%SO_2	STATIC PRESS. (P_s)	VELOCITY HEAD (ΔP_s)	ORFICE PRESS. (ΔH)	IMPINGER TEMP.	DRY GAS TEMP. (T_m)	METERED GAS VOL. (V_m)	SAMPLING RATE
1972	minutes	in. Hg	°F	°F		in. H_2O	in. H_2O	in. H_2O	°F	°F	Cu. ft.	CFM
49 11/16 10:45 am	5.0	29.23	37.4	550	8.7	0		0.85	<50	36.5	2.166	.433
50 11/16 1:45 pm	5.0	29.23	39.2	560	8.5	0		0.9-1.5	<50	41.0	2.394	.479
51 11/16 3:48 pm	5.0	29.23	39.2	560	8.8	+ 0.02		1.0-1.5	<50	44.5	2.462	.492
52 11/17 10:20 am	5.0	29.16	33.8	550	7.1	- 0.05		0.98	<50	36.0	2.327	.465
53 11/17 1:34 pm	5.0	29.16	39.2	560	8.5	- 0.15		0.87-0.9	<50	38.0	2.288	.458
54 11/17 3:35 pm	5.0	29.16	39.2	560	8.8	- 0.28		1.1	<50	40.0	2.495	.499
55 11/20 11:21 am	5.0	29.25	41.0	570	8.2	- 0.19		0.43	<50	39.5	1.533	.307

RUN # DATE TIME	SAMPLING TIME	BAROMETRIC PRESSURE	AMBIENT TEMP.	STACK TEMP. (T_s)	$\%SO_2$	STATIC PRESS. (P_s)	VELOCITY HEAD (ΔP_s)	ORFICE PRESS. (ΔH)	IMPINGER TEMP.	DRY GAS TEMP. (T_m)	METERED GAS VOL. (V_m)	SAMPLING RATE
1972	minutes	in. Hg	°F	°F		in. H_2O	in. H_2O	in. H_2O	°F	°F	Cu. ft.	CFM
56 11/20 2:15 pm	5.0	29.25	41.0	570	8.5	- 0.22		2.40	85	41.0	3.609	.722
57 11/20 4:15 pm	5.0	29.25	41.0	570	8.5	- 0.11		1.40	<50	42.5	3.146	.629
58 11/21 10:27 am	10.0	29.33	38.3	565 560	8.1	- 0.13 0		0.86 0.85	<50 <50	45.0 43.0	4.899	.490
59 11/21 1:30 pm	15.0	29.33	37.4	560 560 560	7.8	- 0.25 - 0.22 - 0.16		0.85 0.85 0.84	<50 <50 60	42.5 44.0 44.5	7.240	.482
60 11/21 3:47 pm	15.0	29.33	39.2	570 570 570	7.9	- 0.03 0 - 0.07		0.85 0.85 0.63	<50 50 75	42.5 46.5 51.0	6.861	.457
61 11/22 10:45 am	15.0	29.22	37.4	550 550 550	7.5	- 0.11 - 0.21 - 0.15		1.90 1.90 1.90	<50 115 85	40.5 48.0 46.0	10.738	.716
62* 11/22 2:30 pm	10.0	29.22	36.5	560 560	7.5	- 0.08 - 0.20		1.30	<50 115	43.5 45.5	6.404	.572

*Pump stopped during run and had to be repaired

RUN # DATE TIME	SAMPLING TIME	BAROMETRIC PRESSURE	AMBIENT TEMP.	STACK TEMP. (T_s)	$\%SO_2$	STATIC PRESS. (P_s)	VELOCITY HEAD (ΔP_s)	ORFICE PRESS. (ΔH)	IMPINGER TEMP.	DRY GAS TEMP. (T_m)	METERED GAS VOL. (V_m)	SAMPLING RATE
1972	minutes	in. Hg	°F	°F		in. H_2O	in. H_2O	in. H_2O	°F	°F	Cu. ft.	CFM
63 12/1 4:00 pm	5.0	28.80	41.9	520	7.4	+ 0.11	0.53	1.60	50	48.5	3.156	.631
64 12/4 10:46 am	10.0	28.96	42.8	540 540	7.8	0.32	0.53 0.54	0.98 1.05	<50 60	41.0 44.5	4.897	.490
65 12/4 4:15 pm	5.0	28.96	42.8	560	8.2	0.19	0.57	0.94	<50	44.0	2.311	.462
66 12/5 11:00 am	15.0	29.08	50.0	540 540 540	8.1	- 0.31	0.59 0.58 0.57	1.20 1.20 1.30	<50 <50 <50	51.5 55.5 58.0	7.830	.522
67 12/5 4:23 pm	15.0	29.08	50.0	540 540 540	8.0	- 0.37	0.57 0.57 0.57	1.55 1.60 1.60	<50 <50 <50	62.5 67.0 70.0	8.838	.589
68 12/6 1:23 pm	15.0	29.30	28.4	475 480 485	9.0 -8.2	+ 1.40	0.49 0.49 0.64	2.20 2.20 2.25	<50 <50 <50	31.5 34.0 35.0	10.406	.694
69 12/7 11:00 am	5.0	29.68	23	555	8.4	+ 0.41	0.50	2.3-2.8	55	39.0	3.816	.763

RUN # DATE TIME	SAMPLING TIME	BAROMETRIC PRESSURE	AMBIENT TEMP.	STACK TEMP. (T_s)	$\%SO_2$	STATIC PRESS. (P_s)	VELOCITY HEAD (ΔP_s)	ORFICE PRESS. (ΔH)	IMPINGER TEMP.	DRY GAS TEMP. (T_m)	METERED GAS VOL. (V_m)	SAMPLING RATE
1972	minutes	in. Hg	°F	°F		in. H_2O	in. H_2O	in. H_2O	°F	°F	Cu. ft.	CFM
70												
12/7				570			0.54	0.42	<50	33.0		
4:21	15.0	29.55	28.4	570	7.4	+ 0.32	0.55	0.41	<50	36.0	4.742	.316
pm				570			0.54	0.41	<50	36.5		
71												
12/11				580			0.54	0.31	<50	29.0		
11:38	15.0	29.61	23.0	580	8.2	+ 0.13	0.53	0.29	<50	32.5	4.215	.281
am				580			0.53	0.29	<50	35.5		
72												
12/11				580			0.51	1.04	<50	31.5		
4:03	15.0	29.60	25.7	580	8.2	- 0.58	0.51	1.05	<50	35.0	6.923	.462
pm				580			0.52	1.05	<50	38.5		

Part B. Laboratory Parameters:

RUN #	PARTICULATES			TRAIN CONFIGURATION MICROGRAMS OF Hg FOUND IN EACH POSITION PERCENTAGE DISTRIBUTION OF Hg IN AMALGAMATORS								TOTAL Hg	Hg CONCENTRATION	
	PROBE AND CYCLONE	FILTER	TOTAL	A	B	C	D	E	F	G	H			
	µg	µg	µg									µg	µg/CF	µg/l
1				H	A 2.24 57.4%	A 0.66 16.9%	A 1.0 25.6%	K	SG			3.90	1.81	0.064
2	1.56			H 2.8	A 4.08 96.7%	A 0.10 2.4%	A <.04 <1%	K <.28	SG			8.86 96.8%	3.10	0.110
3	0.28			S 3.0	A 5.02 85%	A 0.60 10.2%	A 0.28 4.8%	K	SG			9.18	3.04	0.108
4	0.09			H	A 1.7 24.4%	A 4.30 61.7%	A 0.96 13.8%	K	K 0.25	SG		7.30	1.76	0.062
5	0.15			H	A 1.6 47.0%	A 1.12 33%	A 0.68 20.0%	K	K 1.3	SG		4.85	0.76	0.027
6	0.24			H	A 5.0 72.6%	A 0.56 8.1%	A 1.32 19.2%	K 0.10	K 0.50	SG		7.72 92.2%	1.28	0.045
7				E	E	A 2.04 45.5%	A 2.16 48.2%	A 0.28 6.2%	K 0.70	SG		5.18 86.5%	2.00	0.071

RUN #	PARTICULATES			TRAIN CONFIGURATION MICROGRAMS OF Hg FOUND IN EACH POSITION PERCENTAGE DISTRIBUTION OF Hg IN AMALGAMATORS								TOTAL Hg	Hg CONCENTRATION	
	PROBE AND CYCLONE	FILTER	TOTAL	A	B	C	D	E	F	G	H			
	µg	µg	µg									µg	µg/CF	µg/l
8				H 2.08	E	A 2.52 68.1%	A 1.16 31.3%	A 0.02 0.5%	K 0.37	SG		6.15 94.0%	2.57	0.091
9				S 0.44	E	A 0.92 67.6%	A 0.20 14.7%	A 0.24 17.6%	K 0.55	SG		2.35 76.6%	0.95	0.034
10				H-S 0.48	E	A 0.28 4.8%	A 0.56 9.6%	A 5.00 85.6%	K 0.20	SG		6.52 96.9%	2.77	0.098
11				E	E	A 3.70 86.9%	A 0.32 7.5%	A 0.24 5.6%	K 0.59	SG		4.85 87.8%	1.90	0.067
12				E	A 3.0 81.5%	A 0.40 10.9%	A 0.28 7.6%	E	K 1.73	SG		5.41 68.0%	2.14	0.075
13	0.56			A 1.24 28.1%	A 1.42 32.2%	A 1.76 39.8%	E	E	K 0.42	SG		5.40 92.2%	2.14	0.075
14	0.53			H 0.77	E	A 1.40 34.1%	A 0.60 14.6%	A 2.10 51.2%	K 0.67	SG		6.07 89.0%	2.44	0.086

RUN #	PARTICULATES			TRAIN CONFIGURATION MICROGRAMS OF Hg FOUND IN EACH POSITION PERCENTAGE DISTRIBUTION OF Hg IN AMALGAMATORS								TOTAL Hg	Hg CONCENTRATION	
	PROBE AND CYCLONE	FILTER	TOTAL	A	B	C	D	E	F	G	H			
	µg	µg	µg									µg	µg/CF	µg/l
15	0.95			S 0.25	E	A 1.70 23.6%	A 3.15 43.5%	A 2.40 33.1%	K 0.12	SG		8.57 98.6%	3.56	0.125
16	0.55			H-S 0.31	E	A 1.52 21.6%	A 0.90 12.8%	A 4.60 65.5%	K 0.15	SG		8.03 98.1%	3.14	0.111
17	0.25			H 0.25	E	A 3.70 90.9%	A 0.29 7.1%	A 0.08 2.0%	K 0.48	SG		5.05 90.5%	3.91	0.138
18	0.31			H 1.50	E	A 0.44 30.6%	A 0.84 58.3%	A 0.16 11.1%	K 1.20	SG		4.45 73.0%	2.38	0.084
19	0.09			H 0.30	E 0.60	A 0.18 58.0%	A 0.07 22.6%	A 0.06 19.4%	K 0.18	SG		1.48 87.8%	0.48	0.017
20	0.43			H 1.03	E 0.34	A 0.80 45.5%	A 0.68 38.6%	A 0.28 15.9%	K 0.68	SG		4.24 84.0%	1.20	0.042
21	0.81			H 1.86	E 0.19	A 2.75 44.1%	A 3.10 49.7%	A 0.38 6.0%	K 1.29	SG		10.38 87.6%	2.57	0.091

RUN #	PARTICULATES			TRAIN CONFIGURATION MICROGRAMS OF Hg FOUND IN EACH POSITION PERCENTAGE DISTRIBUTION OF Hg IN AMALGAMATORS								TOTAL Hg	Hg CONCENTRATION	
	PROBE AND CYCLONE	FILTER	TOTAL	A	B	C	D	E	F	G	H			
	µg	µg	µg									µg	µg/CF	µg/l
22	0.30			H 0.61	E 0.30	A 1.70 78%	A 0.28 12.8%	A 0.20 9.2%	K 0.48	SG		3.87 87.6%	2.64	0.093
23	0.46			H 1.39	E 0.36	A 1.71 60.0%	A 0.59 20.7%	A 0.55 19.3%	K 1.63	SG		6.69 75.6%	2.68	0.095
24	0.43			H 2.20	E 0.69	A 3.65 93.8%	A 0.19 4.9%	A 0.05 1.3%	K 1.16	SG		8.37 86.1%	2.81	0.099
25	0.31			H 2.08	E 0.36	A 1.85 33.1%	A 3.50 62.5%	A 0.24 4.3%	K 0.44	SG		8.78 95.0%	2.51	0.089
26	0.09			H 0.52	E 0.20	A 1.28 51.6%	A 0.44 17.7%	A 0.76 30.6%	K 0.69	SG		3.98 82.7%	3.78	0.133
27	0.05			H 1.58	E 0.42	A 0.88 24.7%	A 1.40 39.3%	A 1.28 36.0%	K 0.17	SG		5.78 97.0%	3.73	0.132
28	1.49			H 2.57	E 1.01	A 0.84 46.1%	A 0.88 48.4%	A 0.10 5.5%	K 1.57	SG		8.46 81.4%	3.23	0.114

RUN #	PARTICULATES			TRAIN CONFIGURATION MICROGRAMS OF Hg FOUND IN EACH POSITION PERCENTAGE DISTRIBUTION OF Hg IN AMALGAMATORS								TOTAL Hg	Hg CONCENTRATION	
	PROBE AND CYCLONE	FILTER	TOTAL	A	B	C	D	E	F	G	H			
	µg	µg	µg									µg	µg/CF	µg/l
29	1.65			H 1.29	E 0.19	A 3.50 85.4%	A 0.36 8.8%	A 0.24 5.8%	K 0.25	SG		7.48 96.7%	3.60	0.127
30	1.77			H 3.09	E 0.34	A 2.06 62.4%	A 0.74 22.4%	A 0.50 15.1%	K 0.47	SG		8.97 94.8%	2.15	0.076
31	0.08			H 0.20	E 0.05	A 0.10 40.0%	A 0.08 32.0%	A 0.07 28.0%	K 1.41	SG		1.99 29.1%	4.20	0.148
32	0.13			H 0.10	E 0.17	A 0.26 57.7%	A 0.10 22.2%	A 0.09 20.0%	K 1.25	SG		2.10 40.5%	1.29	0.045
33	0.70			H 1.10	E 0.28	A 0.40 50.0%	A 0.22 27.5%	A 0.18 22.5%	K 3.90	SG		6.78 42.5%	2.94	0.104
34	1.45			H 0.05	E 0.15	A 0.22 57.9%	A 0.10 26.3%	A 0.06 15.8%	K(15g) 2.00	SG		4.03 50.4%	0.77	0.027
35	2.75			H 1.18	E 0.51	A 3.55 66.8%	A 0.88 16.6%	A 0.88 16.6%	K(20g) 3.54	SG		13.29 73.4%	1.79	0.063

RUN #	PARTICULATES			TRAIN CONFIGURATION MICROGRAMS OF Hg FOUND IN EACH POSITION PERCENTAGE DISTRIBUTION OF Hg IN AMALGAMATORS								TOTAL Hg	Hg CONCENTRATION	
	PROBE AND CYCLONE	FILTER	TOTAL	A	B	C	D	E	F	G	H			
	µg	µg	µg									µg	µg/CF	µg/l
36	3.00			H 2.92	E 0.33	A 3.85 55.0%	A 1.20 17.2%	A 1.94 27.8%	K(33g) 8.44	SG		21.68 61.1%	2.16	0.076
37	2.03			H 2.63	E 0.26	A(33g) 2.25 44.2%	A(33g) 1.48 29.1%	A(33g) 1.36 26.7%	K(25g) 4.61	SG		14.62 68.5%	1.97	0.069
38	1.88			H 4.46	E E 0.18	A(33g) 1.74 34.0%	A(33g) 2.04 39.8%	A(33g) 1.34 26.2%	K(33g) 5.50	SG		17.14 67.9%	1.66	0.059
39	1.56			H 4.58	E 0.48	E(gw)* 0.11	A(33g) 2.13 49.7%	A(33g) 2.15 50.2%	K(34g) 8.49	SG		19.50 56.5%	2.02	0.071
40	1.51			H 2.24	H 0.19 (GS TIP)	E 0.07	A(33g) 0.74 59.6%	A(33g) 0.50 40.3%	K(34g) 9.13	SG		14.38 36.5%	1.41	0.050
41	0.45			A 1.36 (1.04) 15.3%	A 3.16 (0.04) 35.6%	A 2.46 (0.02) 27.7%	A 0.96 (0.03) 10.8%	A 0.94 (0.03) 10.6%	K(27g) 4.16	SG		14.65 71.6%	2.01	0.071
42	0.70			A 1.91 (0.97) 24.3%	A 1.86 (0.16) 23.6%	A 1.91 (0.04) 24.3%	A 1.04 (0) 13.2%	A 1.14 (0.02) 14.5%	K(16g) 0.72	SG		10.47 93.1%	1.71	0.060

*A 4 cm column of glass wool was packed in "C." This increased pressure drop in the train so much that the pump was at maximum vacuum throughout the run.

RUN #	PARTICULATES			TRAIN CONFIGURATION MICROGRAMS OF Hg FOUND IN EACH POSITION PERCENTAGE DISTRIBUTION OF Hg IN AMALGAMATORS								TOTAL Hg	Hg CONCENTRATION	
	PROBE AND CYCLONE	FILTER	TOTAL	A	B	C	D	E	F	G	H			
	µg	µg	µg									µg	µg/CF	µg/l
43	0.44			A 2.04 68.9%	A 0.44 14.9%	A 0.20 6.8%	A 0.12 4.0%	A 0.16 5.4%	K 2.76	SG		6.16 55.2%	2.35	0.083
44	0.35			A 6.96 (1.55) 63.8%	A 2.06 (0) 18.9%	A 0.50 (0) 4.6%	A 0.88 (0) 8.1%	A 0.51 (0) 4.7%	K(25g) 2.80	SG		15.61 82.1%	3.41	0.120
45	1.60			A 1.13 (1.93) 11.2%	A 2.48 (0.27) 24.5%	A 3.68 (0.04) 36.4%	A 1.38 (0) 13.6%	A 1.44 (0) 14.2%	K(55g) 7.04	SG		20.99 66.5%	1.97	0.070
46	1.68			A 7.18 (3.59) 57.5%	A 2.08 (0.11) 16.7%	A 1.18 (0.05) 9.4%	A 1.14 (0) 9.1%	A 0.90 (0.09) 7.2%	K(63g) 8.88	SG		26.88 67.0%	2.32	0.082
47	0.74			A 3.39 (0.51) 62.1%	A 0.62 (0) 11.4%	A 0.66 (0) 12.1%	A 0.36 (0) 6.6%	A 0.42 (0) 7.7%	K 9.93	K(3%) 3.64	SG	20.27 33.0%	9.47	0.334
48	0.43			A 1.63 (0.04) 32.0%	A 1.82 (0.41) 35.7%	A 0.68 (0.05) 13.4%	A 0.44 (0.05) 8.7%	A 0.50 (0) 10.2%	K(15.5g) 1.58	K(3%) 2.98	SG	10.63 57.1%	4.47	0.158

RUN #	PARTICULATES			TRAIN CONFIGURATION MICROGRAMS OF Hg FOUND IN EACH POSITION PERCENTAGE DISTRIBUTION OF Hg IN AMALGAMATORS								TOTAL Hg	Hg CONCENTRATION	
	PROBE AND CYCLONE	FILTER	TOTAL	A	B	C	D	E	F	G	H			
	µg	µg	µg									µg	µg/CF	µg/l
49	0.50	0.62 (0.0364g)	1.12	A(24g) 6.10 (0.35) 92.2%	A(24g) 0.35 (0) 5.3%	A(24g) 0.04 (0) 0.6%	A(24g) 0.08 (0) 1.2%	A(24g) 0.04 (0) 0.6%	K(15g) 10.45	K(10g) 0.46	SG	18.99 42.5%	8.77	0.310
50	0.45	0.72 (0.0330g)	1.17	A(24g) 3.48 (0.45) 64.0%	A(24g) 0.50 (0.02) 9.2%	A(24g) 1.20 (0) 22.0%	A(24g) 0.10 (0) 1.8%	A(24g) 0.16 (0) 2.9%	K(20g) 3.99	K(10g) 2.40	SG	13.47 52.6%	5.63	0.199
51	0.24	0.82 (0.0229g)	1.06	A(24g) 3.06 (1.02) 47.9%	A(24g) 1.40 (0.02) 21.9%	A(24g) 0.16 (0.02) 2.5%	A(24g) 1.44 (0) 22.6%	A(24g) 0.32 (0) 5.0%	K(25g) 3.45	K(3%) 1.30	SG	13.25 64.2%	5.38	0.190
52	0.44	0.60 (0.0639g)	1.04	H 2.41	E 0.38	A 6.40 (.02) 94.4%	A 0.22 (0) 3.2%	A 0.16 (0.32) 2.4%	K 0.15	K 0.60	S;	11.70 93.6%	5.03	0.178
53	0.42	0.32 (0.0477g)	0.74	H 2.04	E 0.05	A 5.20 (0) 94.8%	A 0.12 (0) 2.2%	A 0.16 (0) 2.9%	K(15g) 0.28	K 0.08	SG	8.67 95.8%	3.79	0.134
54	0.28	0.58 (0.0289g)	0.86	H 1.51	E 0.04	A 0.60 (.02) 41.6%	A 0.48 (0.09) 33.3%	A 0.36 (0.01) 25%	K(15g) 2.99	K 1.73	SG	8.69 45.7%	3.48	0.123
55	0.56	0.40 (0.0165g)	0.96	H 1.52	E 0.03	A 4.98 (0) 88.6%	A 0.32 (0.04) 5.7%	A 0.32 (0) 5.7%	K 0.23	K 0.03	SG	8.43 96.9%	5.50	0.194

RUN #	PARTICULATES			TRAIN CONFIGURATION MICROGRAMS OF Hg FOUND IN EACH POSITION PERCENTAGE DISTRIBUTION OF Hg IN AMALGAMATORS								TOTAL Hg	Hg CONCENTRATION	
	PROBE AND CYCLONE	FILTER	TOTAL	A	B	C	D	E	F	G	H			
	µg	µg	µg									µg	µg/CF	µg/l
56	0.05	0.56 (0.0231g)	0.61	H 3.36	E 0.12	A 11.98 (0) 92.3%	A 0.74 (0) 5.7%	A 0.26 (0) 2.0%	K(25g) 0.22	K 0.38	SG	17.67 96.6%	4.90	0.173
57	0.77	0.48 (0.0393g)	1.25	H 2.40	E 0.45	A 10.18 (0) 90.7%	A 0.86 (0) 7.7%	A 0.18 (0.42) 1.6%	K(25g) 0.13	K 0.03	SG	15.90 99.0%	5.05	0.178
58	0.88	0.92 (0.0972g)	1.80	H 5.40	E 0.07	A 12.00 (0) 93.3%	A 0.70 (0) 5.4%	A 0.16 (0) 1.2%	K(30g) 0.44	K 0.06	SG	20.63 97.6%	4.21	0.149
59	0.68	0.96 (0.1360g)	1.64	H 5.32	E 0.10	A 16.80 (0.03) 91.3%	A 1.08 (0) 5.9%	A 0.52 (0) 2.8%	K(45g) 1.15	K(10g) 0.33	SG	26.97 94.5%	3.72	0.132
60	1.15	2.48 (0.1421g)	3.63	H 3.15	E 0.11	A 13.80 (0) 67.6%	A 5.10 (0) 25.0%	A 1.5 (0) 7.4%	K(50g) 1.30	K(15g) 0.10	SG	28.69 95.1%	4.18	0.148
61	2.80	1.14 (0.1590g)	3.94	H 1.58	E 0.10	A 6.63 (0) 59.3%	A 3.55 (0.05) 31.8%	A 1.00 (0.04) 8.9%	K(80g) 1.08	K(23g) 0.57	SG	18.54 91.1%	1.73	0.061
62	0.45	0.94 (0.1756g)	1.39	H 2.89	E 0.12	A 10.75 (0.03) 74.4%	A 3.1 (0) 21.4%	A 0.60 (0) 4.2%	K(68g) 1.58	K(20g) 0.72	SG	21.18 89.1%	3.31	0.117

RUN #	PARTICULATES			TRAIN CONFIGURATION MICROGRAMS OF Hg FOUND IN EACH POSITION PERCENTAGE DISTRIBUTION OF Hg IN AMALGAMATORS								TOTAL Hg	Hg CONCENTRATION	
	PROBE AND CYCLONE	FILTER	TOTAL	A	B	C	D	E	F	G	H			
	µg	µg	µg									µg	µg/CF	µg/l
63	0.33	0.24 (0.0757g)	0.57	H 3.51	E 0.13	A(30g) 6.70 (0.23) 76.1%	A(30g) 0.10 (0) 1.1%	A(30g) 0.06 (0.04) 0.7%	A(30g) 0.04 (0) 0.4%	A(30g) 1.90 (0) 21.6%	K(20g) <0.04		13.32 99.7%	4.22	0.149
64	0.34	0.38 (0.0813g)	0.72	H 8.90	E 0.11	A(30g) 5.16 (0.02) 86.7%	A(30g) 0.19 (0.01) 3.2%	A(30g) 0.21 (0) 3.5%	A(30g) 0.20 (0.26) 3.4%	A(30g) 0.19 (0) 3.2%	SG		15.97	3.26	0.115
65	0.09	3.46 (0.0469g)	3.55	H 0.63	E 0.19	A(30g) 3.16 (0.01) 82.1%	A(30g) 0 (0) 0%	A(30g) 0 (0) 0%	A(30g) 0.12 (0.01) 3.1%	A(30g) 0.57 (0.02) 14.8%	K(20g) 0.10		8.36 98.8%	3.62	0.128
66	0.32	1.06 (0.0517g)	1.38	H 14.49	E 0.09	A(30g) 22.47 (0.02) 98.7%	A(30g) 0.05 (0.01) 0.2%	A(30g) 0.03 (0.02) 0.1%	A(30g) 0 (0.02) 0%	A(30g) 0.22 (0.04) 1.0%	SG		38.84	4.96	0.175
67	0.66	0.52 (0.0481g)	1.18	H 16.45	E 0.17	A(30g) 21.98 (0.04) 97.1%	A(30g) 0.22 (0.03) 1.0%	A(30g) 0.14 (0.03) 0.6%	A(30g) 0.14 (0.03) 0.6%	A(30g) 0.16 (0.03) 0.7%	SG		40.60	4.59	0.162
68	2.17	0.91 (0.0865g)	3.08	H 3.97	E 0.06	A(30g) 32.73 (0.01) 89.0%	A(30g) 3.78 (0.01) 10.3%	A(30g) 0.13 (0.01) 0.4%	A(30g) 0.12 (0.01) 0.3%	SG			43.91	4.22	0.149
69	0.22	0.30 (0.0903g)	0.52	H 5.52	E 0.11	A(30g) 5.78 (0.01) 84.8%	A(30g) 0.94 (0.02) 13.8%	A(30g) 0.04 (0.02) 0.6%	A(30g) 0.06 (0.02) 0.9%	K(20g) 0	SG		13.04 100%	3.42	0.121

RUN #	PARTICULATES			TRAIN CONFIGURATION MICROGRAMS OF Hg FOUND IN EACH POSITION PERCENTAGE DISTRIBUTION OF Hg IN AMALGAMATORS								TOTAL Hg	Hg CONCENTRATION	
	PROBE AND CYCLONE	FILTER	TOTAL	A	B	C	D	E	F	G	H			
	µg	µg	µg									µg	µg/CF	µg/l
70	0.15	7.76* (0.0800g)	7.91	H 1.69	E 0.04	A(30g) 1.63 (0.02) 79.1%	A(30g) 0.34 (0.02) 16.5%	A(30g) 0.05 (0.02) 2.4%	A(30g) 0.04 (0.02) 1.9%	K(25g) 0.20	SG	11.98 98.3%	2.53	0.089
71	0.08	0.64 (0.0359g)	0.72	H 11.14	E 0.14	A(30g) 4.99 (0.04) 61.5%	A(30g) 0.77 (0.03) 9.5%	A(30g) 0.85 (0.02) 10.5%	A(30g) 0.87 (0.01) 10.7%	A(30g) 0.63 (0.02) 7.8%	SG	20.23	4.80	0.169
72	0.07	0.54 (0.0493g)	0.61	H 13.78	E 0.09	A(30g) 9.24 (0.03) 79.4%	A(30g) 1.43 (0.02) 12.3%	A(30g) 0.33 (0.01) 2.8%	A(30g) 0.35 (0.02) 3.0%	A(30g) 0.29 (0.05) 2.5%	SG	26.25	3.79	0.134

*The filter became wet during this run.

APPENDIX II

RECOMMENDED PROCEDURE

The following is an outline of the recommended procedure as determined in this study, for the analysis of mercury in stack gases of high SO_2 content.

1- Apparatus and Reagents

In addition to the equipment normally used for isokinetic particulate sampling (glass lined probe, weighed filter, filter holder, cyclone, sample box, console with pump, etc.) the following items are required.

a- For Sampling and Cleanup Procedure:

1- Apparatus

Leco induction furnace equipped with a variac

Tank of nitrogen gas equipped with a pressure reducing valve, flow meter and a drying tube packed with magnesium perchlorate.

Bubbler apparatus with at least five interchangeable sample holders

Two female ball joint adapters to fit amalgamators

Two ball joint clamps

Three impimgers - two modified and one Greenburg-Smith

Five amalgamators and "shells"

Gold chips, about 1/16 inch square by 0.007 inch thick, 150 grams required for each run. These should have been fired in a refractory oven at about 600-700°C for a few hours (or overnight) before each run.

Sample containers - 6 oz. and 16 oz. wide mouth jars with lids.

Sample containers for filters - plastic Petri dishes

Graduated cyclinders - 25, 50, and 250 ml

Triple beam balance

Plastic funnel

Quartz wool (available from Perkin-Elmer Corp.)

Dowel rod - ¾ inch diameter by 12 inch long

A piece of stiff (about #10) wire 12 inches long

Clamps and glass connectors to assembly the train

Stirring rod about 18 inches long

Five wash bottles

Tissues for wiping grease off ball joints

Tygon tubing - 5/16 inch O.D. x 10 feet

Masking tape and a marking pen for labeling containers

2- Reagents

Potassium permanganate, reagent grade crystal

Potassium permanganate solution, 3% w/v in 10% HNO_3 freshly prepared

Stannous chloride wash solution, 1% w/v in 2.5% HCl

Hydroxylamine hydrochloride solution, 1% w/v (to remove permanganate stain)

1:3 HNO_3-H_2O wash solution

Acetone

Silica gel, indicating type

Distilled water

b- For Laboratory Analysis of the Samples:

1- Apparatus

Laboratory Data Control Mercury Monitor (or a standard atomic absorption unit equipped for flameless determinations)

0-10 mv recorder

Bubbler apparatus with interchangeable sample holders

Drying tube

Tygon tubing

Syringes - 5 and 10 ml.

2- Reagents

Standard mercury solutions

(A) Stock 1000 ppm mercury standard containing 1% concentrated nitric acid

(B) 1 ppm mercury standard containing 1% concentrated nitric acid prepared fresh weekly

(C) 50 ppb mercury standard containing 1% concentrated nitric acid prepared fresh daily

Stannous chloride solution: mix 200 gram $SnCl_2 \cdot 2\ H_2O$ with 500 ml HCl and dilute to 1 liter with distilled water.

Hydroxylamine hydrochloride solution: dissolve 50 gram $NH_2OH \cdot HCl$ into 500 ml of distilled water.

Magnesium perchlorate

Distilled water

2- Preparation of the Amalgamators

The amalgamators are prepared as follows. A small plug of quartz wool is inserted from the top of the amalgamator tube and pushed into place against the supporting indentations. A length of ¼ inch dowel rod and a piece of stiff wire can be used to help wedge the wool into position. The gold chips are removed from the oven and allowed to cool for at least 5 minutes. The gold chips are then weighed out and about 30 grams of chips poured into each amalgamator using the plastic funnel. The amalgamator may be tapped gently

to help settle the chips against the plug. After filling the amalgamator tubes with the gold chips, the ground glass tapers should be greased and the amalgamator tubes placed in the "shells." If the amalgamators are not to be assembled into the train immediately, the ends should be stoppered as a precaution against contamination.

3- Assembly of the Sampling Train

All glassware should be rinsed before use with the following sequence: 1% $SnCl_2$ in 2.5% HCl, 1:3 HNO_3-H_2O, distilled water and acetone. The glassware should be allowed to dry before placing it into the train.

The probe, cyclone and filter are assembled into the sampling box in the same configuration ordinarily used for taking an isokinetic particulate sample. The impinger and amalgamator sequence is then assembled as follows, starting with the filter:

a) A Greenburg-Smith impinger containing 250 ml of distilled water.

b) An empty impinger

c) Five amalgamators in series, each one containing 30 grams of gold chips.

d) An impinger containing about 250 grams of silica gel.

Each impinger and amalgamator should be labeled with the run number and the position of that unit in the train (e.g. 13-C). The configuration of the recommended sampling train (excluding cyclone) is illustrated in Figure 20.

4- Sampling

After assembling the train a leak check should be performed and the sample box filled with ice and water. From this point on the sampling

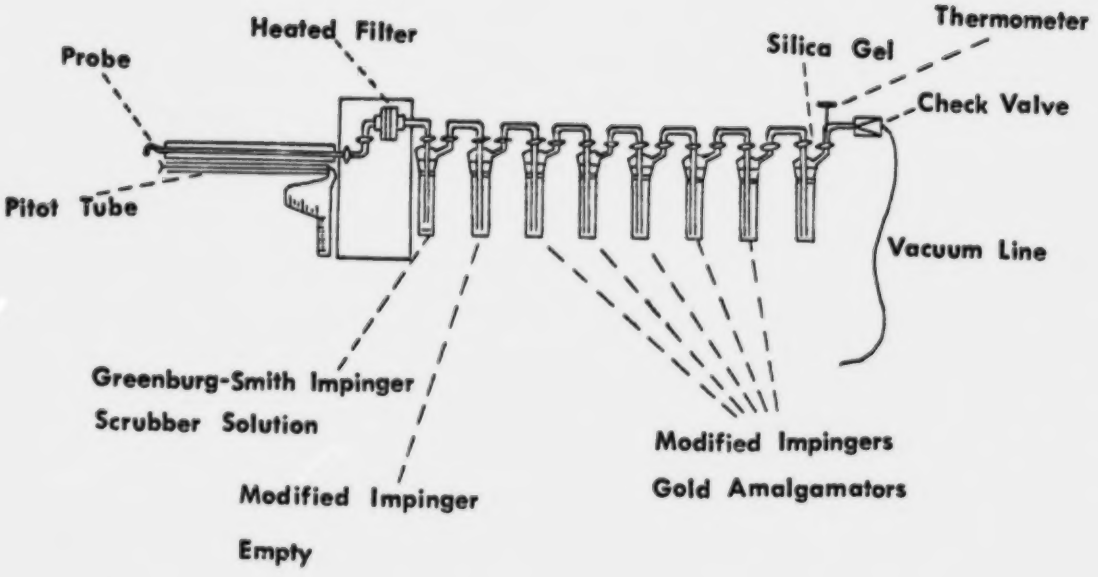

Figure 20. Configuration of the Recommended Sampling Train (excluding cyclone).

procedure and the sample data recorded is the same as for the normal isokinetic procedure as used for particulate sampling. The sample is taken isokinetically for 15 minutes.

5- Cleanup Procedure

After obtaining the sample, the probe and sample box are taken to a suitable are for the cleanup procedure. Distilled water is used for all rinses. Samples are taken from each part of the train ahead of the silica gel and placed in appropriately labeled sample containers as follows:

a) The probe, cyclone and the glass parts of the filter assembly are rinsed into a 16 oz. jar containing 25 ml of the 3% $KMnO_4$ solution.

b) The filter (previously weighed) is placed in a suitable container which is marked with the run number.

c) The inside part of the first impinger (Position A) and the right angle connector leading into it are rinsed into the contents of the impinger "shell." About 7 grams of solid $KMnO_4$ are then added slowly, with stirring, to the liquid in the "shell" until the violet color of the permanganate persists. The solution is then transferred to a 16 oz. sample container and the grams of added potassium permanganate are recorded.

d) The empty impinger and the connector leading into it are rinsed into a 6 oz. sample jar containing 25 ml of the 3% $KMnO_4$ solution.

e) Each of the amalgamator "shells" and the connector leading into that amalgamator are rinsed into separate 6 oz. sample jars, each containing 25 ml of the 3% $KMnO_4$ solution.

f) Each amalgamator is fired into 50 ml of the 3% $KMnO_4$ solution using the apparatus shown in Figure 15. The amalgamators are fired in reverse of their order in the train (i.e. the last one is fired first, the next to the last one is fired second, etc.) in order to minimize contamination of successive samples. The amalgamator is centered in the coil of the induction furnace and connected to the nitrogen

supply and the bubbler with two female ball-joint adapters and two clamps. The nitrogen flow is set at 0.5 liters per minute. The firing is commenced with the variac at a setting of 60% and increased by 5% each minute until the gold is glowing over its entire length. After firing each amalgamator, the sample tube is detached, the drops of permanganate clinging to the bubbler tube are rinsed into it and then the contents of the sample tube are rinsed quantitatively into a 6 oz. sample container. After firing the series of amalgamators, the bubbler apparatus and all the sample tubes are rinsed using the rinse sequence described previously. If any tygon tubing is used between the amalgamator and the bubbler, it should be kept as short as possible and then replaced for each run.

g) A 50 ml blank of the 3% permanganate solution is taken for each run, placed in a 6 oz. sample container and sent to the laboratory along with the samples.

A field record should be kept of all data recorded during the run and of each sample taken for analysis from the train. Upon receipt in the laboratory, each of the samples from the train is diluted to the appropriate volume in a volumetric flask just prior to analysis.

6- Analysis of the Samples

a- Permanganate Solutions

A standard curve is prepared in duplicate for 0.05, 0.10, 0.25, 0.50, and 0.75 µg mercury standards by diluting 1, 2, 5, 10, and 15 ml aliquots of the standard 50 ppb mercury solution to 50 ml. Each standard is placed in an interchangeable sample tube and attached to the bubbler. Three ml of the stannous chloride solution is added with a syringe through the ampoule stopper using sufficient force to mix the solution with the standard. The sample is then aerated (1.4 liter/minute air), volatilizing the mercury which is carried through a drying tube filled with magnesium perchlorate and then through the mercury monitor operated at a 0.64 range setting (least sensitive).

The permanganate samples which contain the mercury from the amalgamators are diluted to 100 ml with distilled water and returned to their containers. (Great care must be taken to rinse the volumetrics with stannous chloride solution between dilutions or cross contamination is observed.) The wash and scrubber solutions are analyzed at the strength at which they arrive from the sampling site. Before each aliquot of sample solution is removed from a jar, the container is shaken thoroughly until all solids are evenly dispersed in the solution. An appropriate sized sample is quickly pipetted from the jar and placed in an interchangeable sample tube where it is diluted to approximately 50 ml with distilled water. Three ml of hydroxylamine hydrochloride solution is added and the tube is swirled until the permanganate color disappears. The tube is then attached to the bubbler and the solution is reduced with three ml of the stannous chloride solution. The mercury is then volatilized by aerating the solution (1.4 liter/minute air). The revolatilized mercury is carried by the air stream through the mercury monitor. All samples should be run in duplicate. The concentrations are calculated from the standard curve and the amount of mercury in each sample is calculated from the dilution factor and the size of the aliquot.

b- Filters

One half of the filter is boiled in 10 ml of concentrated nitric acid for 10 minutes. The filter is disintegrated with a high pressure stream of distilled water and the mixture is diluted to 100 ml. After cooling, the solutions are analyzed by placing 50 ml aliquots in the interchangeable sample tubes and following the sample procedure as is used for

standard solutions.

7- Analysis of the Data

The total amount of mercury found and its distribution in the sample train is obtained from the data determined in the laboratory. This information may conveniently be organized on a data form such as the one shown in Figure 21.

The ratios of t_2/t_1, t_3/t_2, etc. may be calculated for those amalgamators showing sufficient mercury to give a valid value for the ratio. These values may then be compared to give an estimate of the extent of gold contamination occuring during the sampling process. In the absence of such contamination the ratio t_n/t_{n-1} should be about 0.1 or less. In addition the percentage of the total "amalgamator mercury" found on each amalgamator should show an orderly decrease through the train and the percentage found on the last one or two amalgamators should be only one or two percent of the whole (or about the same value as the blank). If these criteria are satisfied, then a collection efficiency of at least 95% may be assumed.

Figure 21. Laboratory Data Form

PLE BER	MILLILITERS TAKEN FOR ANALYSIS	TOTAL VOLUME	MICROGRAMS MERCURY FOUND	TOTAL MICROGRAMS OF MERCURY	BLANK CORR.	NET TOTAL MICROGRAMS OF MERCURY	COMMENTS

APPENDIX III

Isokinetic Data Sheets, Run 72

FIELD DATA

PLANT ASARCO
DATE Dec. 11, 1972
SAMPLING LOCATION Crossover
SAMPLE TYPE Mercury
RUN NUMBER 72
OPERATOR Baldeck & Such
AMBIENT TEMPERATURE 26 °F
BAROMETRIC PRESSURE 29.60
STATIC PRESSURE, (P_s) -.05
FILTER NUMBER (s)

PROBE LENGTH AND TYPE 5'
NOZZLE I.D. .25 inch
ASSUMED MOISTURE, % 5
SAMPLE BOX NUMBER
METER BOX NUMBER
METER $\Delta H_@$ 1.88
C FACTOR .97
PROBE HEATER SETTING 100%
HEATER BOX SETTING 300 °F
REFERENCE Δp

SCHEMATIC OF TRAVERSE POINT LAYOUT

READ AND RECORD ALL DATA EVERY 5 MINUTES

~~TRAVERSE POINT NUMBER~~ Sampling Time	SAMPLING TIME, min / CLOCK TIME (24-hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
				DESIRED	ACTUAL		INLET ($T_{m\ in}$), °F	OUTLET ($T_{m\ out}$), °F			
15 min	Start 4:03	973.439	.51	1.08	1.05	580	26	26	10	280	< 50
	4:08	975.79	.51	1.08	1.04	580	36	27	10	290	< 50
	4:13	978.09	.51	1.08	1.05	580	42	28	10.5	300	< 50
	Stop 4:18	980.362	.52	1.09	1.05	580	47	30	10.5	300	< 50
		(6.923 CF)									
		(0.462 CFM)									

COMMENTS:

$\%SO_2 = 8.2$

Ran slightly under desired ΔH

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4-72

NOMOGRAPH DATA

PLANT ASARCO

DATE Dec. 11, 1972

SAMPLING LOCATION Crossover, Run 72

CALIBRATED PRESSURE DIFFERENTIAL ACROSS ORIFICE, in. H_2O	$\Delta H_@$	1.88
AVERAGE METER TEMPERATURE (AMBIENT + 20°F), °F	$T_{m_{avg.}}$	45°
PERCENT MOISTURE IN GAS STREAM BY VOLUME	B_{wo}	5
BAROMETRIC PRESSURE AT METER, in. Hg	P_m	29.60
STATIC PRESSURE IN STACK, in. Hg ($P_m \pm 0.073$ x STACK GAUGE PRESSURE in in. H_2O)	P_s	-.05
RATIO OF STATIC PRESSURE TO METER PRESSURE	P_s/P_m	.998
AVERAGE STACK TEMPERATURE, °F	$T_{s_{avg.}}$	580
AVERAGE VELOCITY HEAD, in. H_2O	$\Delta p_{avg.}$	.51
MAXIMUM VELOCITY HEAD, in. H_2O	$\Delta p_{max.}$	
C FACTOR		.97
CALCULATED NOZZLE DIAMETER, in.		
ACTUAL NOZZLE DIAMETER, in.		.25
REFERENCE Δp, in. H_2O		

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